HISTORICAL RECONSTRUCTION OF TERRESTRIAL ORGANIC MATTER INPUTS TO FIORDLAND, NZ OVER THE LAST ~500 YEARS

A Dissertation

by

RICHARD WILLIAM SMITH

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

August 2011

Major Subject: Oceanography

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Approved by:

Chair of Committee,	Thomas S. Bianchi
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	Peter Santschi
	Franco Marcantonio
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ABSTRACT

Historical Reconstruction of Terrestrial Organic Matter Inputs to Fiordland, NZ Over the Last ~500 Years. (August 2011)

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Chair of Advisory Committee: Dr. Thomas Bianchi

Fjords contain a significant quantity of sediments deposited in coastal zones over the last ~100,000 years. Studies of Northern Hemisphere fjords have shown that a large part of the high concentration of sedimentary organic matter (OM_{sed}) is terrestrial in origin (OM_{terr}), composed of a modern detrital fraction and an old mineral-associated fraction (OM_{fossil}). These results suggest that fjords are disproportionately responsible, on a per area basis, for the burial of organic matter in coastal zones. This study, after a rigorous examination of CuO and GDGT biomarker methods used to quantify terrestrial organic matter in coastal environments, demonstrated this hypothesis in a Southern Hemisphere fjord system, Fiordland, New Zealand

CuO analysis of Doubtful Sound surface sediments indicated a large contribution of vascular plant material to fjord sediments. The BIT Index correlated strongly with both $\delta^{13}C$ and C/N values in Doubtful Sound surface sediments, indicated that it may accurately trace the relative proportions of marine and soil organic matter (OM_{soil}) in Fiordland. However, a detailed analysis of the conversion of the BIT Index to quantitative estimates of terrestrial (soil) organic matter revealed that these values are

overestimates. Reconstructions of the BIT Index and tetraethers in cores from two locations on the Louisiana continental shelf demonstrated the influence of the crenarchaeol term on BIT Index-based terrestrial organic matter estimates. The differences in the applicability of the BIT Index to these two coastal environments was most likely due to large seasonal changes in productivity on the Louisiana Continental Shelf as well as higher marine relative to terrestrial inputs.

Six cores were reconstructed for contributions from marine OM (OM_{mar}), OM_{fossil}, and $OM_{terrestrial}$ representing the last ~500 years of sedimentation. Spatial variations were larger than temporal variations, owing to negligible development and deforestation in the region. OMterr was the dominant fraction in all but one core, and OMfossil inputs were significant. Additionally, source reconstructions from a variety of biomarkers indicated that Landslides deliver large volumes of detrital organic matter to fjord sediments. These results confirm that fjords bury quantitatively significant volumes of organic carbon on a global scale.

DEDICATION

This dissertation is dedicated to Room 120G. The discussions shared there with friends started my pursuit of knowledge.

This dissertation is also dedicated Kurtis Snyder, you are missed cousin.

And GWAR

ACKNOWLEDGEMENTS

First and foremost I would like to thank those individuals who have shaped who I am as a person: Specifically my parents, Rick and Eileen Smith, my siblings, Chris and Kelly Smith, my advisors, Tom Bianchi and Jim Haynes, and my best friends, Stella Woodard, Matt and Dan Rubin, John Halstead, Brad Brooks, Steve Gilly, and the Montrois brothers. My thanks also extends to my entire large extended family, my committee: Patrick Louchouarn, Mead Allison, Peter Santschi, and Franco Marcantonio, and professors and students I have had meaningful conversations with along the way.

NOMENCLATURE

OM_{terr}	Terrestrial Organic Matter
OM_{sed}	Sedimentary Organic Matter
OM_{mar}	Marine Organic Matter
OM_{fossil}	Fossil Organic Matter
OC	Organic Carbon

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CHAPTER I

INTRODUCTION

Terrestrial Organic Matter Fluxes to Marine Systems

The transport of terrestrial organic matter (OM_{terr}) to coastal sediments represents a significant flux in the global carbon cycle (Raymond and Bauer, 2001). This flux is large enough to account for all the organic carbon (OC) buried in the world oceans (Ludwig et al., 1996). Continental shelves and slopes are the primary sinks for OC in marine sediments (Berner, 1989) due to the constant input of dissolved organic carbon (DOC) and particulate organic carbon (POC) from rivers (Hedges et al., 1997), the former which can be incorporated into sediments via sorption to particulates. Global estimates of riverine DOC and POC fluxes range from 0.25 - 0.36 Pg y^{-1} (Aitkenhead and McDowell, 2000; Meybeck, 1982) and 0.21 Pg y^{-1} (Hedges and Keil, 1995; McKee et al., 2004), respectively, although recent work suggests the total DOC + POC flux is significantly higher, approximately 0.8 Pg C y^{-1} (Richey, 2004). High percentages of riverine carbon fluxes are be terrestrial in origin, including soil organic matter (OM_{soil}) and vascular plant organic matter; however we find much less OM_{terr} in coastal sediments than predicted from riverine fluxes to the ocean (Hedges et al., 1997. This paradox may be in part due to poor estimates of the total flux (Hedges et al., 1997). The complex molecular make-up of the OM_{terr} pool requires the use of a multi-biomarker approach to accurately quantify fluxes from rivers and burial in coastal sediments.

This dissertation follows the style of *Geochimica Et Cosmochimica Acta*.

Biogeochemical, Climatic, and Ecological Impacts

Changes in OM_{terr} burial on glacial-interglacial time-scales have the potential to impact atmospheric CO_2 levels (Burdige, 2005). This pool of organic carbon is considered much more refractory than the more labile marine organic matter (OM_{mar}) pool, such as that derived from photosynthetic carbon leaching from plankton and algae, and so is thought to be preferentially buried on continental shelves and slopes. Approximately one-third of the organic matter buried in marine sediments, primarily in muddy deltaic sediments, is terrestrial in origin (Burdige, 2005). The delivery and burial rates of OM_{terr} to marine sediments, and the potential change in these rates with anthropogenic climate change and watershed modifications have important implications on the flux of CO_2 to the atmosphere.

While OM_{terr} is typically considered resistant to microbial attack relative to OM_{mar}, increasing evidence suggests not only that OM_{terr} inputs to both marine and freshwater trophic systems are underestimated, but may actually be the dominant carbon source utilized by trophic systems under certain environmental conditions (Cole and Caraco, 2001; Cole et al., 2006; Hoffman et al., 2007; Kritzberg et al., 2004; McCallister et al., 2004; McLeod and Wing, 2007; McLeod and Wing, 2009; Moran & Hodson, 1994). Incorporation of OM_{terr} into marine food webs is facilitated in a variety of ways by microbes. Certain microbes are capable of utilizing OM_{terr} in high O_2 environments through enzymes (e.g., phenoloxidase) which can hydrolyze various ringed-compounds in macromolecules (Ander and Eriksson, 1976) such as lignin. The resulting microbial biomass then becomes available to higher consumers. Additionally, microbial activity

enriches the caloric and nitrogen content of detritus, increasing its availability to higher consumers (Mann, 1972).

From an ecological perspective, inputs of OM_{terr} in both dissolved and particulate forms can also have an impact on the turbidity of the water and the size of the photic zone. Turbidity may limit the existence of particulate sensitive organisms such as corals. In New Zealand Fjords, dissolved tannins reduce the penetration depth of light, allowing deep-water organisms, such as black corals, to live at relatively shallow depths.

Bulk Sedimentary Organic Matter Proxies

In the past a variety of bulk OM_{sed} methods have been used to quantify the flux of OM_{terr} to marine sediments, including isotopic ($\delta^{13}C$) and elemental (carbon to nitrogen molar ratios (C/N)) analysis (Bianchi et al., 2007a). OM_{terr} generally has relatively depleted $\delta^{13}C$ values of ~ -26‰ (when inputs of C4 plant material are minimal) while OM_{mar} generated from plankton generally has $\delta^{13}C$ of ~ -18‰ (Sackett and Thompson, 1963). However, terrestrial $\delta^{13}C$ values can be enriched in ^{13}C with the addition of C_4 plant material, which is more enriched than marine carbon (Deines, 1980). OM_{terr} contains the low nitrogen remains of terrestrial organisms, and therefore high C/N ratios can be indicative of a higher proportion of OM_{terr} in the bulk sedimentary organic matter. However, the selective loss of labile N (e.g., amino acids), as well as N enrichment in fine soil particles (Hedges and Keil, 1995) limits the accuracy of this ratio as a sole tracer.

Vascular Plant Biomarkers

The use of organic molecules with a known source, or "biomarkers," has provided researchers with new information on biogeochemical cycling previously unattainable by the bulk analysis of soils, sediments, and water. This is in part due to the large number of different organic molecules found in any one sample, which generally have varying sources, elemental signatures, and degradation rates. However, any biomarker chosen to address a hypothesis is likely only a small portion of the total organic pool. Therefore, a multi-proxy approach, including both biomarkers and bulk elemental properties, is essential in providing accurate interpretations of organic sedimentary records. This can prove to be a large effort, involving high costs and analysis time, as many biomarkers require unique extraction techniques and analytical equipment.

Cupric oxide (CuO) oxidation at elevated temperatures, a technique developed by wood chemists (Pearl and Dickey, 1952; Sarkanen and Ludwig, 1971), was adapted by Hedges and Ertel (1982) to characterize lignin byproducts by gas chromatography/mass spectrometry (GC/MS). CuO oxidation cleaves a large variety of ether and carbon bonds in the lignin macromolecule, releasing phenolic monomer and dimer subunits (Goñi and Hedges, 1992; Hedges and Ertel, 1982). This process also releases other types of molecules that can be quantified and originate from cutin (Goñi and Hedges, 1990a; Goñi and Hedges, 1990b; Goñi and Hedges, 1990c) soil humification processes (Prahl et al., 1994; Houel et al., 1996), and OM_{mar} (Goñi and Hedges, 1995).

Additionally, a suite of benzene carboxylic acids are produced with a variety of potential sources (Dickens et al., 2007).

Vascular plant biomarkers, including lignin and cutin, will be used to quantify vascular plant OC fluxes into Fiordland sediments. Lignin and cutin oxidation products can be accurately quantified through the use of known standards. If soil and vegetation end-member concentrations are measured, the total yearly carbon contribution to sediments can be calculated.

Lignin

Lignin, a polymer found exclusively in vascular plants composed of phenylpropanoid units linked through carbon to carbon (C-C) and ether (C-O-C) bonds (Adler, 1977), is the most abundant aromatic substance in the biosphere (Vicuna, 1988). Due to its refractory nature, lignin can make up a large component of humic substances (Ertel and Hedges, 1985) and is found almost universally in soils (Hedges and Oades, 1997), marine (Gordon and Goñi, 2004; Hedges and Parker, 1976) and lake (Hedges et al., 1982; Hu et al., 1999) sediments. Consequently, lignin has been a useful chemical biomarker for estimating OM_{terr} inputs to coastal regions (Bianchi et al., 2007a; Gordon and Goñi, 2004). Cupric oxide (CuO) oxidation of marine sediments releases three major types of phenols; cinnamyl, vanillyl, and syringyl (Hedges and Parker, 1976), which are indicative of the source and degradation state of the lignin(Hedges et al., 1982). It is also assumed that the abundance of phenols released during oxidation is proportional to the total amount of lignin present in sediment. Using this method, lignin concentration is calculated as the mg of eight types of phenols (vanillic acid, vanillic aldehyde,

vanillone, syringic acid, syringic aldehyde, syringone, cinnamic acid, and ferulic acid) normalized to 100 mg of organic carbon (Λ_8). Another method that has recently gained interest is a thermochemolytic method, which uses tetramethylammonium hydroxide (TMAH) to examine lignin in natural systems such as soils and sediments (Chefetz et al., 2002; Mannino and Harvey, 2000; Nierop and Filley, 2007), and plant litter (Filley et al., 2006).

End-member measurements of cinnamyl, syringyl and vannillyl contents of both woody and non-woody angiosperm and gymnosperm sources have provided a framework for source determination (Hedges and Mann, 1979). However, one must be careful in interpreting this data as vanillyl phenols are more resistant to degradation than syringyl and cinnamyl phenols (Ertel and Hedges, 1984; Hedges and Weliky, 1989). Additionally, end-member values have largely excluded pollen, which has been shown to be more resistant to microbial attack in marine sediments and has very specific lignin signatures (Keil et al., 1998). Finally, the degradation state of lignin in marine sediments can be estimated using the ratio of acid and aldehyde functional groups in vanillyl and syringyl phenols ((Ad/Al)v and (Ad/Al)s, respectively. These ratios increase with increasing oxidative degradation, which can occur by photooxidation (Hernes and Benner, 2002; Opsahl and Benner, 1998), microbial attack under high O_2 conditions (Goñi et al., 1993; Hedges et al., 1988; Hernes and Benner, 2002), or thermal oxidation (Kuo et al., 2008).

Cutin

CuO oxidation of plant material yields a suite of long-chain (primarily C16-C18) hydroxy fatty acids with a cutin origin (Goñi and Hedges, 1990a). Cutin is a polyester biopolymer that protects the aerial parts of soft vascular plant tissue (Martin & Juniper, 1970). Hydroxy fatty acids indicative of a cutin source have been measured in both lacustrine (Cardoso and Eglinton, 1983) and marine environments (Goñi et al., 2000). The original comparative studies of cutin and lignin suggest that lignin is more resistant to degradation and less susceptible to diagenetic alteration of its source signature, and therefore cutin should only be used supplementary to lignin data (Goñi and Hedges, 1990b; Opsahl and Benner, 1995). However, other studies show that cutin gets enriched in soil mineral horizons (Riederer et al., 1993), and may be more diagenetically stable than lignin (Mendez-Millan et al., 2010). Additionally, while lignin distinguishes between woody and non-woody angiosperm and gymnosperm sources, cutin oxidation products, with a wider range of CuO produced constituents, can be used to distinguish between monocots and dicots (Goñi and Hedges, 1990c).

Soil Biomarkers

OM_{soil} represents an estimated ~1400 x 10^{15}g of carbon, a globally significant carbon pool (Gregory and Hinsinger, 1999). Recently, a number of studies have attempted to use specific OM_{soil} markers to distinguish this fraction from bulk OM_{terr} (Kim et al., 2009a; Smith et al., 2010; Walsh et al., 2008).

Glycerol Dialkyl Glycerol Tetraethers (GDGTs)

A biomarker technique originally proposed as a qualitative indicator of the relative amounts of OM_{terr} and OM_{mar} in marine sediments uses the relative abundances of tetraether membrane lipids, specifically GDGTs (Hopmans et al., 2004). As with vascular plant biomarkers, this index has been found to track a particular fraction of the total OM_{terr} pool, in this case OM_{soil} (Walsh et al., 2008). Branched GDGTs are produced in the membrane lipids of anaerobic bacteria found ubiquitously in soils and peat (Weijers et al., 2006a; Weijers et al., 2006b). The amounts of these lipids found in marine sediments are compared to the abundance of crenarchaeol, an isoprenoid membrane lipid found in the Archael bacteria, Crenarchaeota (Sinninghe Damsté et al., 2002). Crenarchaeota have recently been found to be the most predominant prokaryotes in today's oceans, and are ubiquitous in both the waters and sediments of marine and fresh water environments (Hopmans et al., 2004; Powers et al., 2004; Schouten et al., 2000; Schouten et al., 2002; Sinninghe Damsté et al., 2002; Wakeham et al., 2003). The BIT Index in suspended particulate matter and sediments has been shown to decrease from rivers to the continental shelf (Walsh et al., 2008), and has been used as a proxy to trace storm-water (Kim et al., 2007). Additionally, high BIT Index values have been shown to correlate with depleted $\delta^{13}C$ values and high OM_{terr} and *n*-alkane contents in marine sediments (Kim et al., 2006).

Recent studies have called into question assumptions inherent in the BIT Index, and have also started to lay a framework for the particular types of environments it is and accurate proxy in. For example, (Walsh et al., 2008) demonstrates that in peat and

soil-poor environments, the BIT Index does not provide similar estimates of $\%OM_{terr}$ in Northern Hemisphere fjords as Λ_8, $\delta^{13}C$, and C/N analysis. Additionally, it has been shown that the soil and marine GDGTs may vary in their degradation rates and their degree of lateral transport during resuspension or prior to deposition (Huguet et al., 2009; Shah et al., 2008). Therefore, in environments with high amounts of bottom-water advection or conditions promoting fast OM degradation rates, care must be used in interpreting the BIT Index. Finally, marine GDGTs can be added *in situ* by archaeal communities rather than exported from the water column, artificially increasing the marine component (Lipp and Hinrichs, 2009).

3,5-dihydroxybenzoic Acid

3,5 Dihydroxybenzoic acid (3,5-Bd) is not found as a CuO oxidation product of pure plant matter, but is found in soils and marine sediments (Ugolini et al., 1981). When normalized to vanillyl phenols (DHA:V), this proxy correlates with (Ad/Al)v, and also decreases with distance offshore (Prahl et al., 1994). It has therefore been proposed as a marker of soil humification of tannin and other flavenoids (Goñi and Hedges, 1995; Louchouarn et al., 1999). However, this compound has also been produced from CuO oxidation of brown macroalgae (Dickens et al., 2007; Goñi, 1992). Despite this, the DHA:V index has proved useful as a OM_{soil} biomarker (Goñi et al., 2000; Louchouarn et al., 1999; Sánchez-García et al., 2009).

New Zealand Fjords

Fjords are deep, glacially carved estuaries located in high latitudes of both the Northern and Southern Hemisphere. This method of formation leads to a unique

morphology characterized by steep valley walls. Fjords contain a sill at the mouth, and oftentimes multiples sills are present separating various basins within the fjord. Temperate Fjords are estimated to contain at minimum 12% of the organic carbon buried over the last 100,000 years in continental margins (Nuwer and Keil, 2005). Additionally, up to 76% of Fjord organic carbon may be terrestrial in origin (Walsh et al., 2008). Therefore the flux of OM_{terr} into fjords is significant when considering global carbon budgets.

Fiordland, New Zealand is an area comprising 14 fjords on the southwestern tip of the southern island of New Zealand. Large annual rates of rainfall (6200-8000 mm y^{-1}) (Sansom, 1984) coupled with steep topography and periodic seismic events (Keefer, 1994) lead to large inputs of OM_{soil} and intact plant material to the fjord from the surrounding slopes. High sedimentation rates in deeper areas of the fjord (84-430 cm/103 yr in 200-250 m depth) have been shown to contain high amounts of terrestrial components, based on C/N analysis (R. J. McLeod, *unpublished data*). Two recent studies show strong evidence that OM_{terr} entering Doubtful Sound is the dominant carbon source utilized by the local trophic systems (McLeod and Wing, 2007; McLeod and Wing, 2009).

Hypothesis and Approach

Fiordland is a unique setting for examining OM_{terr} inputs to estuarine systems. The steep slopes on these fjords, high regional rainfall, and tectonic activity all allow for non-point and more dramatic point-source inputs from land-slips into these largely understudied fjords. To this end, the purpose of this study is to determine the spatial

distribution and historical changes in OM_{terr} entering Fiordland fjords. The overarching hypothesis is that *high rainfall rates and mass-wasting events in Fiordland's intact watershed create large fluxes of OM_{terr} fjord sediments, which when applied to the total area of Southern Hemisphere fjord sediments represents a significant organic carbon sink relative to global coastal zones.*

This study will use a multi-disciplinary approach that includes: (1) use of radioisotopes to quantify sediment accumulation rates and seabed mixing to develop accurate geochronologies at sites where cores are collected, (2) down-core and spatial analysis of lipid, vascular plant, and soil biomarker compounds and stable isotopes to apportion the sources of vascular plant and soil inputs to fjord sediments, and (3) extensive analysis of soil and vegetation end-members to make quantitative statements on total carbon burial. The specific objectives for this work are to determine:

1) The regional quantitative flux of OM_{terr} into Fjordland and associated carbon burial rates, which may be applicable to other fjord environments, and may help to better constrain global flux estimates;

2) Relationships between transport mechanisms and OM_{terr} accumulation in the fjords over time, by comparing graphs of rainfall, seismic activity, plant and soil biomarker abundance and characteristics, BIT indices, and bulk OM_{sed} proxies in cores from multiple fjords representing the last ~300 years of sediment accumulation;

3) Future predictions on changes in OM_{terr} burial in Fjordland estuaries based on climate change induced precipitation anomalies.

Significance

Biogeochemical perturbations brought about by climate change are an important current issue in multiple fields. To fully understand how all chemical cycles, especially carbon, will react to changes in temperature and precipitation we must look to the large sinks – in this case the coastal ocean. The flux of OM_{terr} to the coastal ocean must be accurately quantified due to its relatively refractory nature and tendency to accumulate in coastal sediments. The flux of OMterr to the coastal ocean represents a "bottleneck" in the modern active organic carbon cycle and is the only modern avenue towards preservation (Hedges, 1992). To accurately quantify this flux, it is necessary to measure it in a variety of environments in both the northern and southern hemispheres. The bulk of the biogeochemical fjord literature focuses on fjords in the northern hemisphere (Nuwer and Keil, 2005; Walsh et al., 2008). However, northern hemisphere fjords are closer to the pole and therefore have experienced glaciation more recently and have less developed soils. Therefore, this dissertation work will take place in Fiordland, New Zealand, a remote southern hemisphere fjord system with an intact temperate rainforest watershed. This will be the first biogeochemical work of its kind in a southern hemisphere fjord system. Additionally, the cores used for this study are the first ever taken in many of the fjords.

In addition to the uniqueness of performing this study in Fiordland and the implications for global carbon cycling, the BIT Index is still in the beginning stages of its progression as a biomarker. This study will use the BIT Index along with other well-established biomarkers to confirm a complex hypothesis.

CHAPTER II

A COMPARISON OF LIGNIN PHENOLS AND BRANCHED/ISOPRENOID TETRAETHERS (BIT INDEX) AS INDICES OF TERRESTRIAL ORGANIC MATTER IN DOUBTFUL SOUND, FIORDLAND, NEW ZEALAND

Introduction

The transport of terrestrial OM (OM_{terr}) to coastal sediments represents a significant flux in the global carbon cycle (Ludwig et al., 1996; Raymond and Bauer, 2001). Fluvial transport of OM_{terr} alone represents a flux of 4×10^{14} g C yr^{-1} to the global ocean (Schlesinger and Melack, 1981). To fully estimate how coastal sedimentary organic matter (OM_{sed}) would respond to changing climatic conditions, it is necessary to accurately quantify inputs, sources, and sedimentary preservation and remineralization of OM_{terr}. Much less OM_{terr} is found in coastal sediments than predicted from riverine fluxes to the ocean, due in part to poor estimates of total riverine flux (Hedges et al. 1997 and references therein). Therefore, quantifying techniques need to be revised, either by adding new OM_{terr} abundance proxies (such as biomarkers) to compare with older markers, or by providing additional data from under-studied coastal regions of the globe.

Lignin, a macromolecule found exclusively in vascular plants, is often measured in coastal sediments to provide information on terrestrial plant input (see Bianchi et al., 2007b and references therein). The use of lignin phenols produced by CuO oxidation has been the most commonly chosen method for determining lignin abundance, source

and degradation state (Hedges and Ertel, 1982). For example, the method allows differentiation of woody and non-woody sources of angiosperms and gymnosperms (Ertel and Hedges, 1984). Additionally, as lignin is degraded, acidic aromatic chain functional groups are produced from aldehyde functional groups (Hedges et al., 1986) and become relatively more abundant. Therefore, ratio values of acidic to aldehyde (Ad/Al) functional groups are calculated as a proxy for lignin degradation state in vanillyl and syringyl phenols [(Ad/Al)v and (Ad/Al)s, respectively]. Another method that has recently gained interest is a thermochemolytic method, which uses tetramethylammonium hydroxide (TMAH) to examine lignin in natural systems such as soils and sediments (Chefetz et al., 2002; Mannino and Harvey, 2000; Nierop and Filley, 2007; Wysocki et al., 2008) and plant litter (Filley et al., 2006).

Another biomarker technique recently proposed is an indicator of the relative amounts of soil and marine OM in marine sediments. This proxy, the branched/isoprenoid tetraether (BIT) index (Hopmans et al. 2004), uses the relative abundances of two types of glycerol dialkyl glycerol tetraethers (GDGTs) in marine sediments. Branched GDGTs are membrane lipids from an unknown type of anaerobic bacteria found ubiquitously in soils and peat (Weijers et al. 2006a, b). The amounts of these lipids found in marine sediments are compared with the abundance of crenarchaeol, a membrane tetraether lipid with a unique cyclohexyl moiety found in Crenarchaeota, a phylogenetic group in Archaea (Damste et al., 2002). Crenarchaeol occurs ubiquitously in both the marine water column as well as in marine and lake sediments, hot springs and soils (Schouten et al., 2000; Schouten et al., 2002; Sinninghe

Damste et al., 2002; Wakeham et al., 2003; Hopmans et al., 2004; Powers et al., 2004). Pure marine OM, in which only crenarchaeol (GDGT IV) is present, would have a theoretical BIT value of 0, while pure soil OM, in which only the branched GDGTs are present, would have a theoretical BIT value of 1. Deviations from the terrestrial end member exist because of the presence of small to moderate amounts of crenarchaeol in soils and peat (Weijers et al., 2006b; Kim et al., 2006). The BIT index in suspended particulate matter and sediments has been shown to decrease from rivers to the continental shelf (Hopmans et al., 2004; Kim et al., 2006; Walsh et al., 2008), and has been used as a proxy for tracing river flood events (Kim et al., 2007) and OM_{soil} deposition into coastal oceans (Herfort et al. 2006). Additionally, high BIT index values have been shown to correlate with depleted $\delta^{13}C_{org}$ values and high OM_{terr} and *n*-alkane content in marine sediments (Kim et al., 2006). Using a three end member mixing model, the BIT index, along with $\delta^{13}C_{org}$ and n-alkane/alkenone values allows the separation of soil, plant and marine OM inputs in marine sediments (Weijers et al. 2009).

The major goal of this study was to determine whether BIT index values correlate or not with lignin phenol abundance in surface sediments from Doubtful Sound, a New Zealand fjord. These biomarkers were also compared with bulk OM properties ($\delta^{13}C$ and C/N). Proxy comparisons were made for both shallow and deep water surface sediments from different locations in Doubtful Sound, varying in distance from the sill. Biomarker distributions with depth and distance from headwater streams were compared to give insight into potential differences in sources, hydrodynamic sorting and diagenesis. However, the primary focus was on method comparison.

Methods

Site Description

Doubtful Sound is a fjord in Fiordland National Park on the southwest coast of the South Island of New Zealand (Fig. 1). This pristine estuarine coastal region offers a

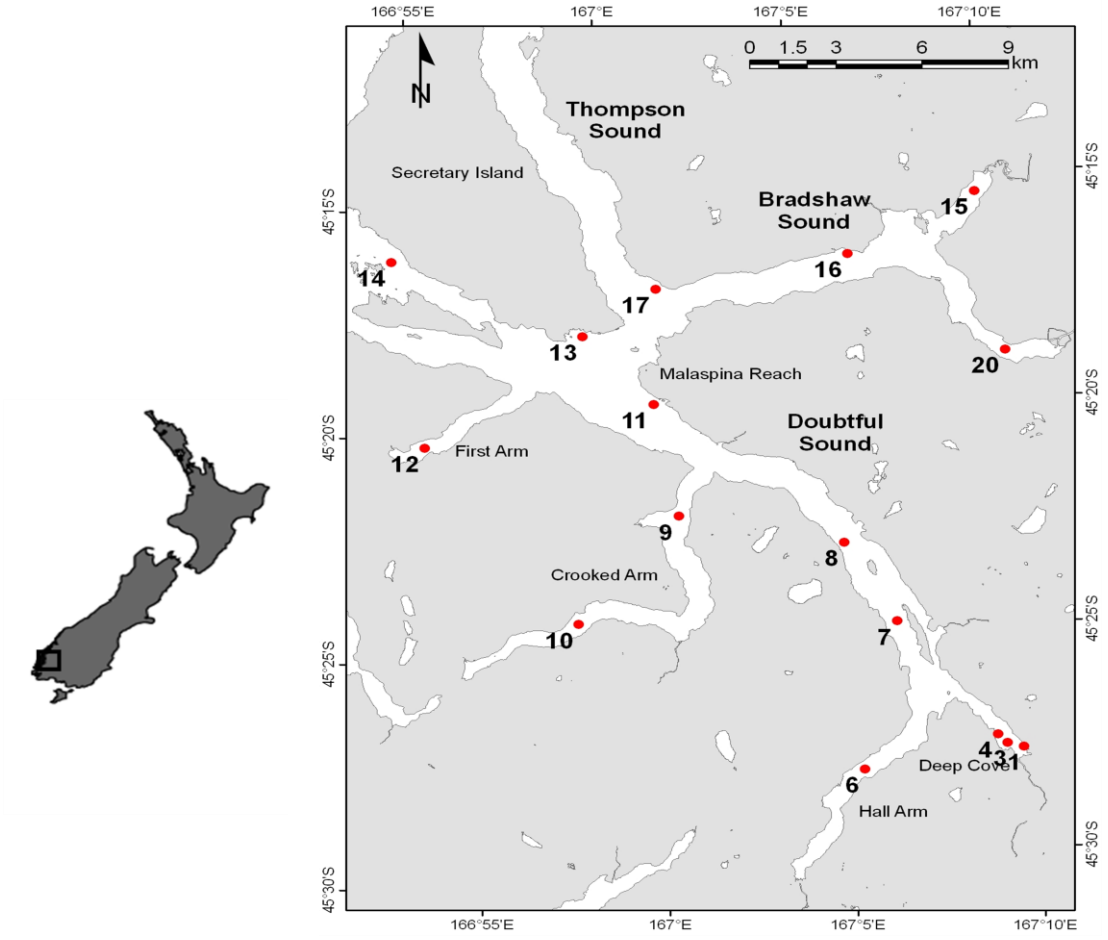

Figure 1. Fiordland National Park. Shown are sixteen locations at which 0-2 cm sediment surface intervals were sampled.

unique opportunity to study pristine sediments with high OM_{terr} burial and preservation rate as a result of relatively high sedimentation rate and the occurrence of anoxic bottom water in the deeper parts of the basins. High sedimentation rates are a result of periodic mass-wasting events, in which soil, trees and the associated understory vegetation fall into the fjord (Whitehouse 1988; Keefer, 1994), as a result of both high rates of rainfall and seismic activity (Keefer, 1994). Bottom water anoxia occurs because of a strong halocline and bathymetric sills preventing bottom water mixing. OM_{terr} input to the fjords has been a recent topic of interest, as it has been shown to be an important contributor to the food web in Doubtful Sound and surrounding fjords in (McLeod and Wing, 2007). In fact, New Zealand has been found to have some of the highest erosion rates in the world (Hicks et al., 1996). Some of these high rates of erosion result from high relief, shallow soil (Ahnert, 1970, Willet and Brandon, 2002) and a rainfall rate that averages 7 m $year^{-1}$ (Hicks et al., 1996).

Sediment Samples

Van Veen grab samples ($0.1m^2$) were collected throughout Doubtful Sound and nearby fjords and core sub-samples from the surface sediments (0-2 cm) were taken. The presence of bacterial mats at the water-sediment interface attests to the collection of the surface sediments. This was also verified using naturally occurring radionuclide downcore profiles of ^{210}Pb and ^{137}Cs (M. Allison, University of Texas, unpublished data). Sampling locations included a range from the mouth to the head of the estuary, as well as its upstream reaches. 16 sediment samples were collected for both BIT and lignin phenol analysis from the sound (Fig. 1). Numbered locations on the map are

given a ‘DS’ prefix in the text and tables. Two additional surface sediment samples were collected from Doubtful Sound in Malaspina Reach and Deep Cove (Fig. 1) (MR2, DC1 respectively) that were not analyzed for tetraethers, as well as one surface sediment sample from both Broughten Arm (BA1) and Dusky Sound (SC2), located within fjords to the south of Doubtful Sound. These are not shown on Fig. 1 as lignin-phenol and BIT comparisons were not made. However the values are included in lignin interpretations. For biomarker depth comparisons, differences were made between shallow and deep sites, with the cutoff depth as follows: shallow (19, 38, 42, 43, 64, 76 m) and deep (94, 96, 135, 142, 182, 185, 279 m) sites in Doubtful Sound. Differences in average depth between shallow ($x = 50.8 +/- 21.3$, $n = 7$) and deep ($x = 158.9 +/- 59.3$, $n = 7$) sites are significant ($p < 0.05$, *t*-test). Only sites for which both lignin and GDGT data are available are used for the comparison. Soil (S1, S2, S3, S4) and leaf-litter (LL1, LL2, LL3) samples were obtained close to Doubtful Sound using grab sampling. These samples were obtained from the headwater regions of the fjord as well as some of areas where the forest could be accessed from the shoreline. All samples were shipped from the University of Otago in dry ice and were kept frozen at Texas A&M University. Sediments were freeze-dried and homogenized with a mortar and pestle prior to BIT, lignin phenol, and bulk carbon analyses.

Bulk Isotope and Elemental Analysis

Total organic carbon (OC), total nitrogen and stable carbon isotope analyses of sediments were carried out by T. Boutton, Stable Isotope Laboratory, Department of Ecosystem Science and Management at Texas A&M University. Measurements were

made using an elemental analyzer (Carlo Erba EA-1108; CE Elantech, Lakewood, NJ) interfaced with an isotope ratio mass spectrometer (Delta Plus, Thermo Electron, Waltham, MA) operating in continuous flow mode. Carbon isotope ratios were calculated in δ notation as follows:

$$\delta = [(R_{sample} - R_{STD})/R_{STD}] \times 10^3 \quad (1)$$

where, R_{STD} is the $^{13}C/^{12}C$ ratio of the Vienna Pee Dee Belemnite (V-PDB) standard (Coplen, 1996) and R_{sample} is the $^{13}C/^{12}C$ ratio of the sample. The precision of duplicate measurements was +/- 0.1‰. C/N values are calculated as molar ratios. While Perdue and Koprivnjak (2007) show the misuse of this proxy as an OC tracer and suggest using N/C ratios, C/N ratios are still used, as conversions to % OM_{terr} from end-members are not made.

BIT Index

Ca. 1 to 4 g sediment were extracted (3 x, 5 min each) in 9:1 dichloromethane (CH_2Cl_2):methanol (CH_3OH) using a Dionex accelerated solvent extractor (ASE) at 100^{o}C and 7.6 x 10^6 Pa. The extracts were loaded onto an activated (2 h, 150 ^{o}C) alumina pipet column. Four column volumes of 9:1 hexane:CH_2Cl_2 were used to elute the apolar fraction and 3 of 1:1 CH_2Cl_2:MeOH to elute the polar fraction, which contained the GDGTs. Polar extracts were dissolved in ~1 m hexane/isopropanol (99:1; % vol:vol). Aliquots (100 µl) were placed into silianized 150 µl vial inserts and analyzed according to Hopmans et al. (2004). Analysis were performed with a Shimadzu 2010A Series liquid chromatography-mass spectrometry (LC-MS) instrument with LCMSsolution software. Separation was achieved on a Prevail Cyano column (4.2

x 150 mm, 3 μm; Alltech) maintained at 30^{o}C. GDGTs were eluted at a flow rate of 1 ml min^{-1}, first isocratically with hexane/isopropanol (99:1; % vol:vol) for 5 min, then with a linear gradient up to 1.8% isopropanol over 40 min. After each analysis the column was cleaned by backflushing 10% isopropanol for 10 min. Detection was achieved using atmospheric pressure chemical ionization-mass spectrometry (APCI-MS) of the eluent using the following conditions: nebulizer pressure 65 psi, vaporizer temperature 400 ^{o}C, N_2 drying gas flow 2.5 l min.$^{-1}$ at 220 ^{o}C, capillary voltage -4.5 kV. Single ion monitoring (SIM) was used instead of full scanning due to increased reproducibility and signal-to-noise ratio (Schouten et al. 2007). SIM was set to scan $[M+H]^+$ of crenarchaeol (1292) and the three $[M+H]^+$ ions of the branched GDGTs (1050, 1036 and 1022), with a dwell time of 100 ms for each ion. Recent studies (Schouten et al., 2009; Escala et al., 2009) have shown that BIT indices vary significantly among laboratories as a result of MS sensitivity differences among molecules of varying MW (i.e. terrestrial GDGTs vs crenarchaeol). Therefore, a sample with a previously measured BIT value was analyzed every 8 injections to ensure consistency in our laboratory. An example chromatogram is provided in Fig. 2. Labeling of branched GDGTs (I – III) and crenarchaeol (IV) are consistent with the structures and labeling in Hopmans et al. (2004).

The average relative standard deviation (%) of BIT index, based on 3 extraction replicates, was 0.4 %. Absolute amounts of GDGTs are not known because of a lack of a quantitative standard. The BIT index was calculated according to Hopmans et al. (2004).

Lignin Phenols

Freeze-dried sediment containing 3 to 5 mg OC were analyzed for lignin phenols using the CuO method of Hedges and Ertel (1982) as modified by Goñi and Hedges

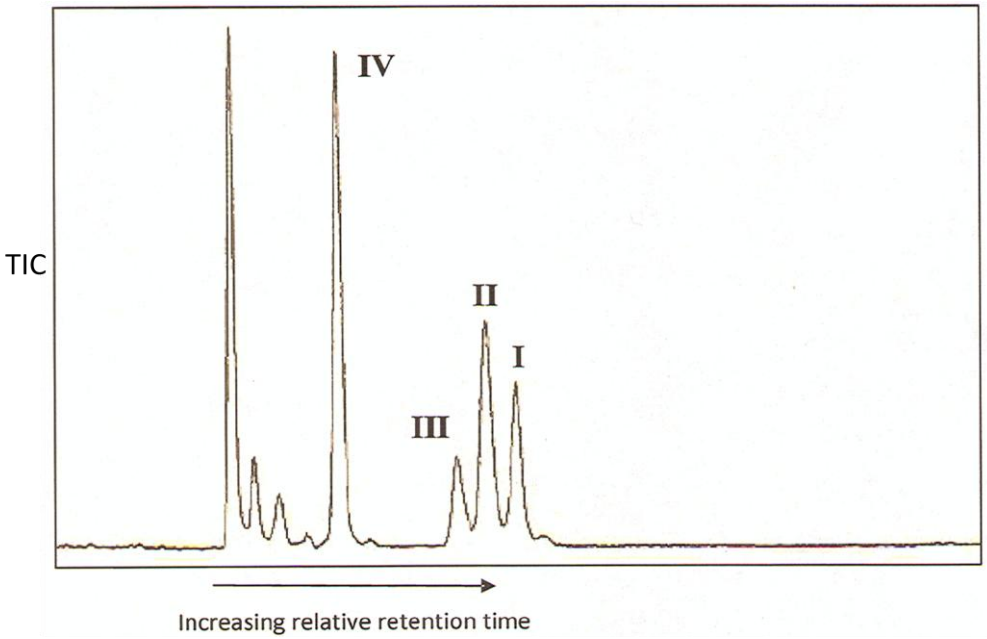

Figure 2. LC/MS glycerol dialkyl glycerol tetraether (GDGT) chromatogram. The total ion count (TIC) shown was the sum of 8 GDGTs scanned for in SIM mode. Labeled GDGT peaks include those used in the branched/isoprenoid tetraether (BIT) index. Compound labeling (I – IV) is consistent with GDGT labeling in Hopmans et al. (2004); IV is the marine crenarchaeol GDGT, while peaks I – III represent the branched terrestrial GDGTs.

(1992). Sediments were transferred to stainless steel reaction vials and digested with 330 mg (+/- 4 mg) CuO in 2N NaOH under N_2 at 150 ^oC for 3 h. Reaction products were allowed to cool and extracted with three successive 3 ml aliquots of Et_2O (peroxides removed), filtered through combusted glass fiber, dried under N_2, reconstituted in pyridine and converted to trimethylsilyl derivatives using bis-(trimethylsilyl)trifluoroacetamide (BSTFA). Lignin phenol derivatives were analyzed using an Agilent 6890n gas chromatography instrument/ coupled to an Agilent 5973N mass spectrometry instrument (GC-MS).

Quantification and of lignin phenols was based on an ethyl vanillin internal standard and a mixed standard (containing known amounts of all lignin reaction products of interest) was analyzed with each batch of 12 samples batch to determine new response factors. Λ_8 values were calculated as the mg sum of 8 lignin phenols [3 syringic phenols (S), 3 vanillylic phenols (V), cinnamic aldehyde and ferulic aldehyde (C)] per 100 mg OC^{-1}. Individual phenols include vanillin (VAL), acetovanillone (VON), syringealdehyde (SAL), vanillic acid (VAD), acetosyringone (SON), syringic acid (SAD), 4-hydroxybenzaldehyde (PAL), 4-hydroxyacetophenone (PON), *p*-hydroxybenzoic acid (PAD), 3, 5-dihydroxybenzoic acid. (3,5-Bd), *p*-hydroxycinnamic acid (CAD) and ferulic acid (FAD). The acid to aldehyde ratios of both vanillic and syringic phenols were used as indicators of lignin degradation state. S/V values vs. C/V values were plotted as indicators of lignin source. The relative standard deviation of Λ_8 values from duplicate extractions ranged from 0.8 to 3.9%, and that of individual phenol concentrations from 1.4 to 6.9%.

Statistics

Simple regression analyses were performed using Sigma Plot, Inc. (Version 11.0). Means are reported with a 95% confidence interval and differences between means were established using unpaired *t*-tests (Sokal and Rohlf, 1995). One-way analysis of variance (ANOVA) was performed using Sigma Plot Inc., (Version 11). An *F*max test was used prior to ANOVA and regression analyses to check for homogeneity of variances. This test uses the ratio of the maximum and minimum variances and then compares the ratio with the cumulative probability distribution of *F*max to determine homogeneity of variances (Sokal and Rohlf, 1995).

Results

Bulk OC

The average amount of OC (% w/w) in samples decreased significantly from leaf litter (40.6 +/- 4.4 %, n = 3) to soil (10.7 +/- 3.6 %, n = 5) ($p < 0.001$) and from soil to sediments (5.3 +/- 3.4 %, n = 20) ($p = 0.004$), which contained up to 11.4 % and as little as 0.6 % OC (Appendix A, B).

Bulk $\delta^{13}C$ values of end members, both soil and leaf litter, were not significantly different (p 0.220). Therefore, the depleted $\delta^{13}C$ values for both Fiordland soil (-29.8 +/- 0.9 ‰, n = 5) and leaf-litter (-30.6 +/- 0.7 ‰, n = 3) were averaged to give an estimate of the bulk $\delta^{13}C$ signature of OM_{terr} in the region (-30.1 +/- 0.9 %, n = 8). Fjord surface sediments were significantly ^{13}C enriched (-26.9 +/- 1.2 ‰, n = 20) compared to the terrestrial end member value ($p < 0.001$) and had a range of OM signatures from predominantly terrestrial (-28.7 ‰), based on terrestrial end-members, to more ^{13}C

enriched values (-24.3 ‰; Appendix A), indicating increased inputs of marine carbon. Ranges of $\delta^{13}C$ values are similar to those found in Northern Hemisphere fjords (Huguet et al., 2007; Smittenberg et al., 2005; Breugel et al., 2005).

C/N values for sediments ranged from 5.7 to 36.8 (20.1 +/- 7.5, n = 16) (Table 1). The highest values, 36.8 and 26.3 at sites 1 and 4, respectively, were located in close proximity to runoff from a local hydroelectric power plant. The lowest values, 16.2 and 14.7 at sites 11 and 13, respectively, were found in sediments from the widest area of the fjord, close to the mouth.

No significant difference was found in surface sediment C/N values, bulk $\delta^{13}C$ and OM content averages at shallow (<90 m) and deep (>90 m) sites (Appendix C).

Abundance, Composition, and Degradation State of Lignin

Average Λ_8 values were not statistically different between leaf litter (8.62 +/- 4.26, n = 3), soil (6.24 +/- 6.37, n = 4) and sediment (6.76 +/- 2.27, n = 20) samples (p = 0.587, one way ANOVA). However , the sediment samples exhibited a much smaller range than the three leaf litter and four soil samples, which had Λ_8 values as high as 12.5 and 16.6, respectively (Appendix A, B). Λ_8 values for Doubtful Sound surface sediments ranged from 2.73 to 11.2, indicating a spatially heterogenous distribution of plant OM input. Λ_8 values at shallow (6.74 +/- 2.24, n = 7) and deep water (5.30 +/- 1.68, n = 7) sites were not significantly different (p = 0.198; Appendix C).

Average C/V and S/V ratio values for lignin in sediments, soils and leaf litter did not vary significantly (p = 0.109, One Way ANOVA). However, two soil samples, S1 and S2, had significantly different C/V and S/V values from the rest of the samples,

indicating mixed lignin sources (Fig. 3). C/V and S/V values for sediment samples ranged from 0.05 to 0.66 (0.10 +/- 0.13) and 1.00 to 1.34 (1.22 +/- 0.11), respectively (Appendix A). The source plot indicated that the predominant source of lignin in soils and sediments was woody also angiosperms (Fig. 3). However, one sediment sample (DS07) had S/V and C/V values indicating non-woody angiosperms as the predominant source of lignin.

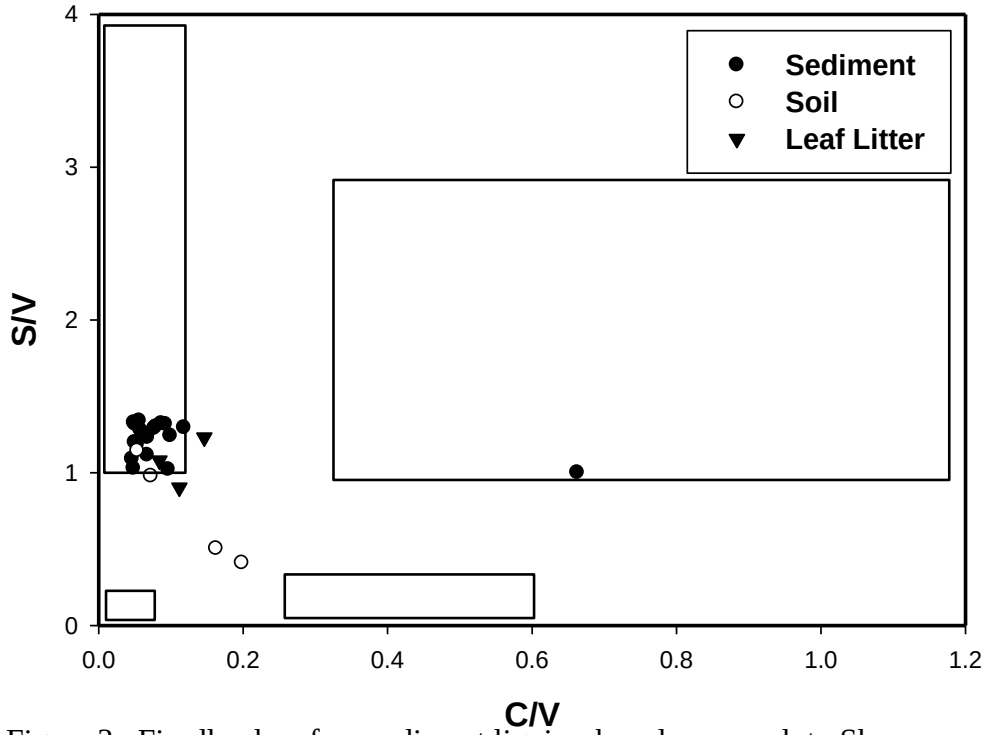

Figure 3. Fiordland surface sediment lignin-phenol source plot. Shown are syringyl to vanillyl (S/V) phenol abundance vs. cinnamyl to vanillyl (C/V) phenol abundances obtained from cupric oxide (CuO) oxidation of Fiordland leaf litter, soil and sediment samples. The boxes represent known ranges of S/V vs. C/V for woody and non-woody gymnosperms and angiosperms. Designations are as follows: woody angiosperm (A), non-woody angiosperm (a), woody gymnosperm (G), and non-woody gymnosperm (g).

On average, Ad/Al values of lignin for sediments, soils and leaf litter were all relatively low, indicating fresh or preserved lignin. Leaf litter end members, representing the freshest pool of lignin, had average (Ad/Al)s and (Ad/Al)v values of 0.15 +/- 0.01 and 0.16 +/- .00 (n = 3), respectively. As indicated by the small standard deviations, these two parameters were very similar for all three leaf litter samples, providing an end member estimate of lignin "freshness" before it enters soil or fjord sediments. Ad/Al values for soil samples were as high as 0.30 in vanillyl phenols and 0.24 in syringyl phenols, and one sediment sample had a very degraded signature (DS07; 0.97 and 0.99 for vanillyl and syringyl phenols, respectively). While no significant difference was found between average Ad/Al values (for both phenol types) in soils and sediments, both of these lignin sinks contained significantly higher averages than leaf litter.

BIT Index

The average BIT index decreased significantly from soil to sediments ($p = 0.001$). No crenarchaeol was present in Fiordland soils, so all soil samples had a calculated BIT index of 1.00, consistent with the soil end member found in Hopmans et al. (2004). BIT values in Doubtful Sound surface sediments, ranging from 0.24 to 0.93 (0.57 +/- 0.24) (Appendix A), indicated large variations in the relative amounts of OM_{soil} and OM_{mar}, based on soil end members and an assumed marine end member of 0 (Hopmans et al., 2004). Sites 1 and 16 both had a value of over 0.9 (Appendix A). Site 1 receives large freshwater input (~450 $m^3 s^{-1}$) from a local hydroelectric power plant

that drains a large catchment in the upstream reaches of the fjord. Site 16 is, however, located in a more downstream area in the fjord (Fig. 1).

Biomarker Comparisons

Λ_8 values did not correlate significantly with C/N values (R^2 0.005, p 0.776, n = 20). The correlation contained, however, six sediment samples not used in the BIT index correlation with the same bulk sediment proxy. Removing these samples and only using sediments for which BIT values were provided did not increase the significance of the correlation (R^2 0.010, p 0.710, n = 14). Λ_8 values showed a better correlation with $\delta^{13}C$ values (R^2 0.191, p 0.054, n = 16), although the correlation was still not significant. However, in this case we did find a significant correlation with Λ_8 and $\delta^{13}C$ values when the data were reduced to only those samples for which we have BIT index data (R^2 0.320, p 0.022, n = 14).

BIT indices showed increased correlations with both $\delta^{13}C$ values (R^2 0.774, p <0.001, n = 14) and C/N values (R^2 0.629, p <0.001, n = 14) as compared to Λ_8 correlations with the same bulk proxies. When plotted against each other, BIT index and Λ_8 values showed a weak correlation (R^2 0.313, p 0.038, n = 14). Additionally, the highest BIT value and Λ_8 value for sediments were both from at Site 16, located in the upstream reaches of Doubtful Sound.

Biomarker Spatial and Depth Variation

A transect was chosen for spatial analysis starting at DS01, near the stream-fed head of the fjord and ending at DS14, near the mouth. This transect included, in order of stations, DS01, DS03, DS04, DS07, DS08, DS11 and DS14. DS01 was chosen to be the

"0 km" point and, for spatial analysis, distances were estimated for all other transect stations from this point. Both BIT and $\delta^{13}C$ values showed strong terrestrial signals at DS01 (0.92 and -28.7 ‰, respectively) with an increasing marine influence towards the mouth. $\Lambda 8$ values did not show this trend until the fourth site, DS07. C/N values also did not show the trend until the third site (DS04). All four proxies showed an increase in the OM_{terr} component at station DS14.

BIT indices in shallow water (< 90 m) surface sediments (x = 0.70 +/- 0.23, n = 7) were significantly higher than those located at deeper water (< 90 m) sites (x = 0.44 +/- 0.17, n = 7; Appendix C). No significant difference was found between these two depth groups in lignin and bulk carbon parameters.

Discussion

Source and Diagenetic State of OM_{terr}

C/V and S/V ratios indicated that woody angiosperms were the dominant source of lignin for all surface sediments in Doubtful Sound. Cinnamyl as well as syringyl oxidation products can be depleted relative to vanillyl oxidation products if the lignin has undergone extensive degradation (Bianchi et al., 2002). However, it was likely that our S/V and C/V ratios had not been skewed by selective degradation due to low Ad/Al ratios and a dominance of C_3 plants in the watershed. However, DS07, with high Ad/Al ratios and a unique source signature, may have been diagenetically altered. The role of landslides in delivering large point-source amounts of vegetation, including trees, understory, leaf litter and detritus to the sound may be reflected in the variable, but often large, amount of undegraded woody plant tissue in surface sediments, and high Λ_8

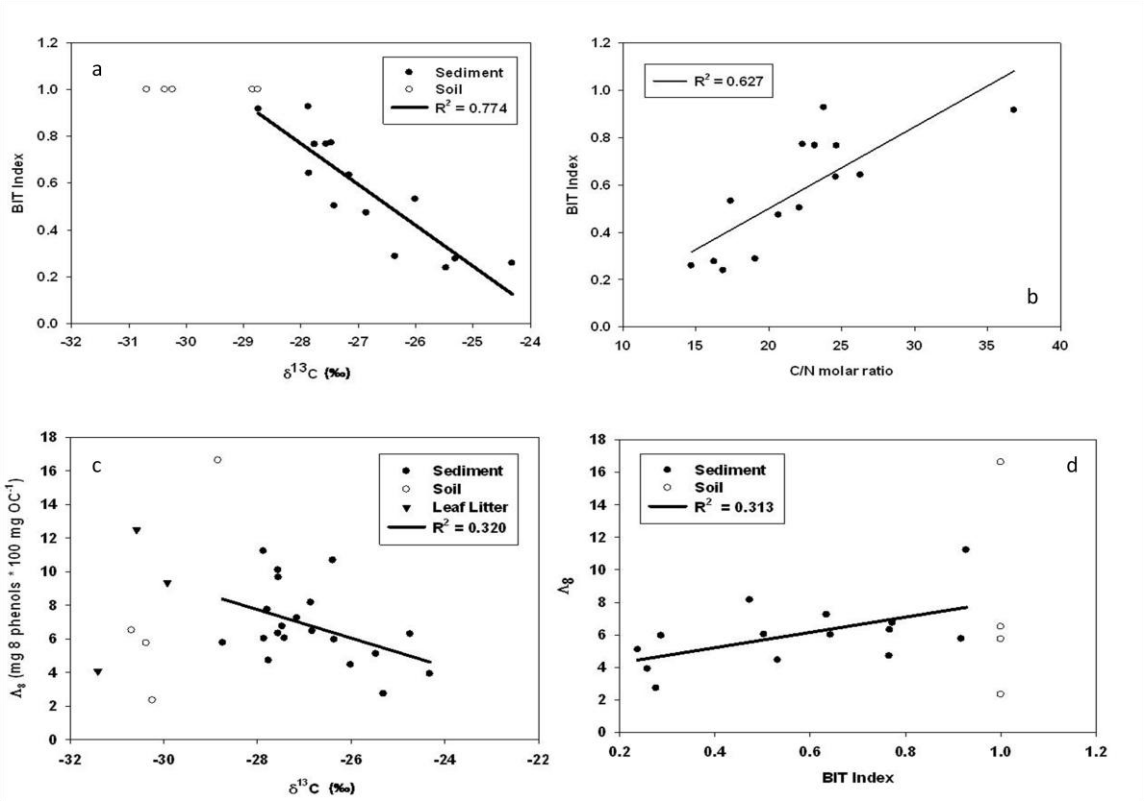

Figure 4. Linear regressions of bulk organic carbon proxies and biomarkers. a) BIT index vs. $\delta^{13}C$, b) BIT index vs. C/N, c) Λ_8 vs. $\delta^{13}C$, d) Λ_8 vs. BIT index.

values relative to other coastal, non- fjord studies. Ad/Al values of both syringyl and vanillyl phenols show that pre-depositional decay was minimal, but moreover that post-depositional decay may also not be very high, with the exception of one sample location. However, since (Ad/Al) values do not increase during anaerobic oxidation of lignin (Hamilton and Hedges, 1988), we cannot determine whether or not the lignin had undergone degradation after it made it to the deeper fjord sediments.

Λ_8 vs. Bulk Carbon Parameters (C/N, $\delta^{13}C$)

The only significant correlation between lignin abundance and terrestrial/marine signatures of bulk carbon parameters was between Λ_8 values and $\delta^{13}C$ among 14 surface sediment samples (Fig. 4). The most likely scenario for the scatter observed and the resulting weak, but significant, correlation, is the wide range of Λ_8, relative to $\delta^{13}C$ values, found in soil and leaf litter samples.

BIT Index vs. OM_{terr} Proxies

Soil end members and sediment BIT index values vs. C/N and $\delta^{13}C$ values showed a clear, significant linear mixing line from pure terrestrial OM to a mix of marine organic matter (OM_{mar}) and OM_{terr} (Fig. 4). This is the first study, to our knowledge, in which such a strong significant correlation has been found between the BIT index and C/N values, although a previous study has also found a strong relationship between the BIT index and $\delta^{13}C_{org}$ values (Kim et al. 2006).

A weak trend exists between the magnitude of the BIT index and Λ_8 in Doubtful Sound sediments, suggesting that, while to some extent these biomarkers behave similarly, the biomarkers involved in these two proxies vary significantly in their (i)

transport mechanisms to sediments, (ii) degradation during transport and burial and/or (iii) sources. A majority of lignin transported to fjord sediments may be from large mass-wasting events, in which vegetation and leaf litter were transported, intact to the fjord, after which they began to degrade and concentrate lignin in surface sediments. These events in any one area may be few and far between, causing OM_{soil} from large rain events to be the predominant type of OM in fjord sediments. Therefore, bulk carbon parameters will reflect OM_{soil} input rather than bulk lignin input. Recent work in Vancouver Island fjords found that lignin phenols did not correlate with the BIT index (Walsh et al., 2008). Additionally in that study no correlation was found between BIT index and bulk carbon parameters. The authors attributed this to the lack of developed soil and peat in the local watershed. Although New Zealand fjords receive large inputs of undegraded woody lignin, as indicated by high Λ_8 and low Ad/Al values, the significant correlation of BIT values with bulk carbon parameters suggests that OM_{soil} represented the dominant fraction of OM_{terr} delivered to the sediment. If the dominant source of lignin to fjord sediments was plant matter that had already been incorporated into the sediment through leaching and degradation, we would expect a better correlation between the BIT index and Λ_8 values, as their source would have been consistent. Additionally, this lack or correlation may have been due to a greater "patchiness" in soil lignin abundance than in terrestrial GDGT abundance. This conclusion needs more soil and leaf litter end members for further corroboration.

Spatial and Depth Trends

Significantly higher BIT values in shallow water surface than in deep-water sediments were not reflected in Λ_8 values, possibly suggesting that these two proxies were subjected to differences in hydrodynamic sorting mechanisms. The intensity of transport events may also have had a role here. More woody material may have been deposited into the deeper basins from the steep slopes of the fjord during periodic mass-wasting events. This is in contrast to the more gradual overland flow of soil erosion and riverine inputs that allowed accumulation of OM_{soil} in the shallower regions. Additionally, as no significant differences were found between shallow and deep sediments in bulk carbon parameters, GDGTs may have been differentially associated between particulate and dissolved phases, compared to the bulk OM pool. Finally, degradation can be one or two orders of magnitude greater in oxic than anoxic environments, and favors the enrichment of terrestrial, or branched GDGTS, relative to crenarchaeol (Huguet et al., 2009), resulting in larger BIT values. However, shallow water surface sediments have not likely been degraded post-deposition extensively enough to account for the observed differences in the Bit Index values.

BIT and $\delta^{13}C$ values revealed high concentrations of terrigenous material at the head of the fjord, that were quickly diluted by OM_{mar} even in nearby stations (Figure 5). Λ_8 values did not show this trend at the beginning of the transect; however a decreasing trend towards the mouth of the fjord starts at 10 km away from DS01. The BIT index, a proxy for only the soil component of the total OM_{terr}, indicates that the headwater stream feeding the fjord is responsible for delivering large amounts of OM_{soil} that either settles

quickly or becomes significantly diluted by a marine component (crenarchaeol) within a short distance. The role of hydrodynamic sorting in transporting and separating out bulk components has been shown in coastal areas dominated by large rivers (Bianchi et al., 2002). While headwater streams in Fiordland do not have as large annual discharges as large rivers, high annual rainfall rates, known to occur in periodic intense events, may have resulted in higher than normal discharge rates and increased levels of

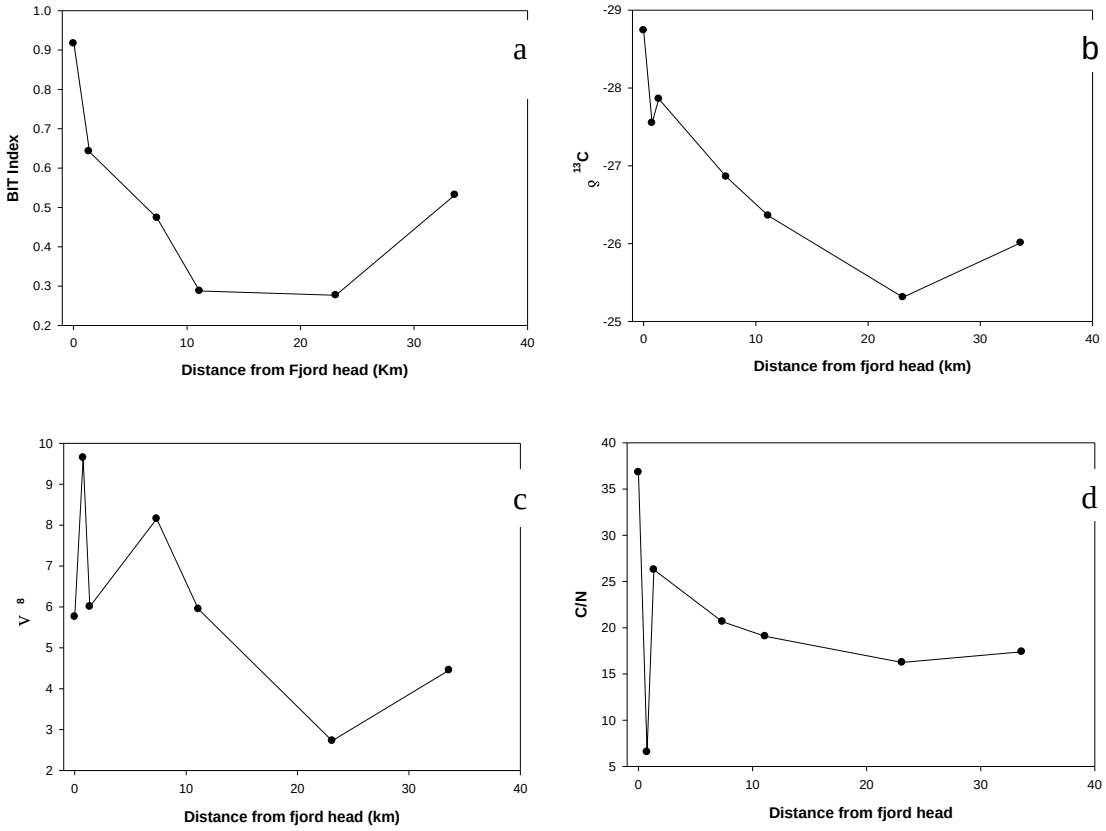

Figure 5. Doubtful Sound surface sediment transect. a) Branched/isoprenoid tetraether (BIT) index, b) $\delta^{13}C_{org}$ (‰), c) Λ_8 (mg 8 lignin-phenols/100 mg OC), and d) C/N molar ratios. The x-axis in all four graphs represents the distance from station DS01, arbitrarily chosen as 0 km.

hydrodynamic sorting of OM_{terr}. Because of the similarity in $\delta^{13}C$ values with distance from DS01, it is reasonable to suggest that OM_{soil} is concentrated in the upper reaches of the fjord. These data also support the role of headwater streams in transporting significant amounts of OM_{terr} to the upper estuary.

Conclusions

A weak correlation between Λ_8 and BIT index values suggested differences in the relative amounts of lignin and terrestrial GDGTs input to NZ fjords by the dominant regional OM_{terr} transport mechanisms. 7 m of annual rainfall delivered large amounts of OM_{soil} via slope runoff and headwater streams to fjord sediments. While non-point source inputs throughout the entire estuary are responsible for delivering the bulk of the OM_{soil}, large amounts of undegraded lignin in deeper basins may have originated from mass-wasting events. The linear correlation between the BIT index and bulk carbon parameters was a result of the areal extent of a forested catchment, steep fjord slopes, and high annual rainfall rates, all of which resulted in inputs of large amounts of OM_{soil}. The results highlight the importance of using multiple biomarkers due to variations in OM_{terr} sources. Further study is needed to better estimate the occurrence, size and distribution of mass-wasting events in these fjords, as well as their impact on biogeochemical cycling in Fiordland.

CHAPTER III

A RE-EVALUATION OF THE USE OF BRANCHED GDGTS AS TERRESTRIAL BIOMARKERS: IMPLICATIONS FOR THE BIT AND TEX_{86} INDICES

Introduction

Terrestrial organic matter (OM_{terr}) derived from rivers and coastal erosion is typically a complex mixture of both woody and non-woody vascular plant debris and mineral associated soil organic matter (OM_{soil}) (Bianchi and Canuel, 2011 and references therein). Multi-proxy approaches have become increasingly common to distinguish OM_{soil} from vascular plant detritus (OM_{VPD}) organic fractions on continental shelves (Kim et al., 2006; Huguet et al., 2007; Walsh et al., 2008; Belicka and Harvey, 2009; Kim et al., 2009a; Weijers et al., 2009; Schmidt et al., 2010; Smith et al., 2010); where the majority of sedimentary organic matter (OM_{sed}) is buried in the global ocean (Berner and Lasaga, 1989; Hedges, 1992). Stable carbon isotopic signatures ($\delta^{13}C$) have been successfully used in coastal regions, but suffer from the wide range of values found in C_3 and C_4 plants (Gordon and Goñi, 2004; Bianchi and Canuel, 2011). The most common biomarkers to date to differentiate organic matter sources in marine sediments are lignin-phenols produced from alkaline CuO oxidation of lignin macromolecules (Hedges and Ertel, 1982). While the relative abundance of the various lignin-phenols produced provide information on source and diagenetic state of vascular plant material (Hedges and Mann, 1979; Hedges et al., 1988), it is impossible from this method alone to quantify the relative amounts of OM_{soil} and OM from $OM_{VPD.}$ In order to accomplish

this without implementing a separate analytical technique, 3,5-dihydroxybenzoic acid, a CuO oxidation product derived from the humification of tannins and other flavenoids, is normalized to the sum of vanillyl phenols (3,5Bd:V) as a qualitative indicator of the relative amount of OM_{soil} present (Prahl et al., 1994). A more recent study suggests that the ratio of hydroxylated to non-hydroxylated benzene carboxylic acids ($BCA^{OH}/BCA^{no\text{-}OH}$) is higher in soils than in fresh plant material and OM_{sed}, and therefore may be used as an additional CuO OM_{soil} proxy (Dickens et al., 2007). However, most non-lignin CuO products have been identified in multiple terrestrial sources, and therefore it is necessary to develop the use of biomarkers identified only in soils.

Core-lipid branched glycerol dialkyl glycerol tetraethers (brGDGTs; structures I-III, Hopmans et al. (2004)), are produced with glucuronosyl and glucosyl headgroups ("parent" molecules) (Liu et al., 2010) by a yet unknown group of soil anaerobic bacteria, possibly Acidobacteria (Peterse et al., 2010). These bacteria have been shown to be ubiquitous in peat and soils (Damste et al., 2000; Schouten et al., 2000; Hopmans et al., 2004; Weijers et al., 2006b, 2007; Huguet et al., 2010a), as well as in marine and lacustrine environments associated with the deposition of OM_{soil} (Schouten et al., 2007; Belicka and Harvey, 2009; Blaga et al., 2009; Kim et al., 2009a; Powers et al., 2010; Smith et al., 2010). Preliminary evidence suggests possible production in the water column of lakes based on the degree of methylation and cyclization of brGDGTs in soils vs. lake waters as well as anomalously high concentrations in lake sediments (Tierney and Russell, 2009; Tierney et al., 2010). Due to the large amount of OM_{soil} relative to organic matter derived from peat delivered to the sea by large rivers, brGDGTS provide

a specific tracer for soil-derived organic matter on continental shelves. In addition to having a unique source, they have been shown to degrade slower than lignin (Huguet et al., 2008).

Hopmans et al. (2004) introduced the branched/isoprenoid tetraether (BIT) Index, a proxy for OM_{soil} that normalizes the abundance of brGDGTs to crenarchaeol, a tetraether membrane lipid synthesized by group 1.1b crenarchaeota (Sinninghe Damsté et al., 2002; Pitcher et al., 2010). Due to the widespread occurrence and high abundances of crenarchaeota, crenarchaeol has ubiquitously been identified in the water column and sediments of marine and lacustrine environments, and is even produced to a minor degree in soils (Schouten et al., 2000,2002; Powers et al., 2004; Weijers et al., 2006a,b; Blaga et al., 2009; Damste et al., 2009; Tierney and Russell, 2009; Powers et al., 2010). The BIT Index ranges from 0 to 1, with a value of 0 indicating the presence of pure OM_{mar} with no terrestrial inputs, and a value of 1 is the theoretical end-member for soils. The soil end-member can be less than 1 due to the production of small to moderate amounts of crenarchaeol in soils (Weijers et al., 2006b). BIT Index values are generally low on continental shelves, and increase towards the mouths of large rivers (Kim et al., 2006; Walsh et al., 2008; Kim et al., 2009a). The Index has seen increasing use in separating OM_{soil} from OM_{VPD} as a quantitative proxy for $\%OM_{soil}$ (Belicka and Harvey, 2009; Kim et al., 2009a; Weijers et al., 2009; Schmidt et al., 2010).

Recent studies have revealed discrepancies between the BIT Index and vascular plant biomarkers in sediments (Huguet et al., 2007; Walsh et al., 2008; Belicka and Harvey, 2009; Weijers et al., 2009; Schmidt et al., 2010; Smith et al., 2010). In this

study, evidence from branched and isoprenoidal GDGT and CuO biomarker profiles from four cores taken from the Louisiana Continental Shelf (LCS), Gulf of Mexico, USA (along with comparisons of GDGT-based mixing models) are used to show that the BIT Index may be inaccurate in some circumstances as a OM_{soil} proxy, and that brGDGTs should be considered as a OM_{soil} biomarker without normalization to crenarchaeol. These results provide the first detailed explanation of the non-linearity of the BIT Index and the influence of the crenarchaeol term on $\%OM_{soil}$ estimates in marine sediments, which have been suggested in previous literature as inherent bias in the index (Herfort et al., 2006; Huguet et al., 2007, 2008; Walsh et al., 2008; Belicka and Harvey, 2009; Weijers et al., 2009; Schmidt et al., 2010), and also suggests a more accurate calculation substituting brGDGT concentrations.

Methods

Site Description and Sampling

For the past few decades there has been considerable interest in understanding the source and fate of OM_{terr} delivered to the LCS (Hedges and Parker, 1976; Hedges and Vangeen, 1982; Goñi et al., 1997; Gordon and Goñi, 2003, 2004; McKee et al., 2004; Corbett et al., 2006; Bianchi et al., 2007a,b; Sampere et al., 2008; Bianchi et al., 2009). The Mississippi River Delta is one of the most anthropogenically modified river systems in the world, and the shelf experiences the largest hypoxic events in the Western Hemisphere (Rabalais et al., 2002a; Rabalais et al., 2002b; Syvitski et al., 2009; Bianchi et al., 2010).

Four box-cores were collected on two 2008 Mechanisms Controlling Hypoxia

(MCH) cruises aboard the *R/V Pelican* along the 20 m isobath south of Atchafalaya Bay on the LCS (Fig. 6). Sites 8C and BC1 were sampled during MCH11 in April ($8C_{apr}$ and $BC1_{apr}$), and again in July ($8C_{july}$ and $BC1_{july}$). Sediments were immediately sectioned into 2 cm intervals down to ~20 cm and frozen until analysis. These sites are outside of the primary depositional path of the Mississippi and Atchafalaya Rivers (Corbett et al., 2006, 2007; Allison et al., 2000; Neill and Allison, 2005). Therefore some of the muds

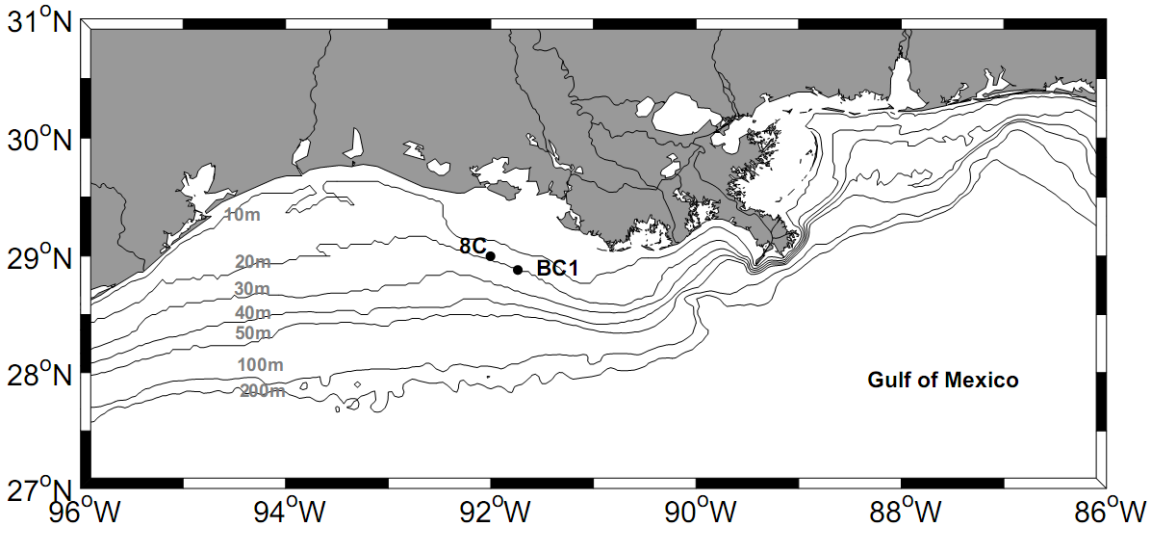

Figure 6. The Louisiana Continental Shelf and Louisiana Coastline. Shown are the three stations cores were retrieved from for this study.

in these regions may represent old deltaic lobe sediments that have been exposed due to low sedimentation rates and a net erosion of fresh surface muds. Thus, these sediments

are very different than the organic-rich mobile mud belts to the east, where much of the suspended sediments are deposited along the 50 m isobath in the primary depositional pathway (Corbett et al., 2006, 2007; Sampere et al., 2008).

CuO Oxidation and GC/MS Analysis

Freeze-dried sediment containing 3 to 5 mg OC were analyzed for lignin monomers and 3,5-dihydroxybenzoic acid using the CuO method of Hedges and Ertel (1982) as modified by Goñi and Hedges (1992). Briefly, sediments were transferred to stainless steel reaction vials and digested with 330 mg (+/- 4 mg) CuO in 2N NaOH under N_2 at 150 ^{o}C for 3 h. Reaction products were allowed to cool, extracted with three successive 3 mL aliquots of diethyl ether (peroxides removed with ferrous ammonium sulfate dissolved in water), dried with sodium sulfate, evaporated under a stream of N_2, reconstituted in pyridine, and converted to trimethylsilyl derivatives using bis-(trimethylsilyl)trifluoroacetamide (BSTFA) at 70^{o}C for 1 hour. Oxidation products were analyzed using an Agilent 6890n gas chromatography instrument/ coupled to an Agilent 5973N mass spectrometry instrument (GC-MS).

Compound identification of lignin-phenols was made by comparison with pure standards. Quantification and % recovery of oxidation products was based on an ethyl vanillin (EVAL) internal standard. The relative response factors (RRFs) to EVAL for all compounds were calculated from a mixed standard analyzed with every batch of 12 samples. The mixed standard contained vanillin (VAL), acetovanillone (VON), vanillic acid (VAD), syringaldehyde (SAL), acetosyringone (SON), syringic acid (SAD), *p*-coumaric acid (CAD), ferulic acid (FAD), *p*-hydroxybenzaldehyde (PAL), *p*-

hydroxyacetophenone (PON), *p*-hydroxybenzoic acid (PAD), and 3,5-dihydroxybenzoic acid (3,5-Bd). RRFs were calculated using the pure compounds in the mixed standard.

All compound yields are normalized to mass (mg g^{-1}: Σ) (Appendix A). Lignin concentrations are calculated as the yield of S, V, and C phenols per 10 g of sediment ($\Sigma 8_{10}$) and used as a proxy for OM_{terr} (precision, based on coefficient of variation (CV), less than 5% in selected triplicate runs). Sediment mass normalized concentrations of 3,5-Bd (3,5:g) are used as a proxy for OM_{soil} (Prahl et al., 1994). Acid to aldehyde ratios of vanillyl phenols are used as indicators of lignin degradation state ([Ad/Al]v (Hedges et al., 1988). The lignin-phenol vegetation index (LPVI) was first introduced by Tareq et al. (2004) and is used as an indicator of lignin source.

GDGT Isolation and LC/MS Analysis

GDGTs were analyzed according to Hopmans et al. (2004), as modified by Smith et al. (2010). Ca. 1 to 4 g of sediment were extracted (3X, 5 min each) in 9:1 CH_2Cl_2:CH_3OH using a Dionex accelerated solvent extractor (ASE) at 100 ^oC and 7.6 x 10^6 Pa. The extracts were loaded onto an activated (2 h, 150 ^oC) alumina pipet column. Hexane:CH_2Cl_2 (9:1 vol:vol) was used to elute the apolar fraction and CH_2Cl_2:MeOH (1:1) to elute the polar fraction, which contained the GDGTs. Polar extracts were dissolved in hexane/isopropanol (99:1; % vol.:vol.) at a concentration of 2 mg mL^{-1}, and filtered through a 0.2 µM PTFE syringe-tip filter into silianized 150 µL vial inserts.. Analysis were performed with a Shimadzu 2010A Series liquid chromatography–mass spectrometry (LC–MS) instrument with LC-MS solution software. Separation was

achieved with a Prevail Cyano column (4.2 x 150 mm, 3 µm; Alltech) maintained at 30 ^{o}C. GDGTs were eluted at a flow rate of 1 mL min.$^{-1}$, first isocratically with hexane/isopropanol (99:1; %vol.:vol.) for 5 min., then with a linear gradient up to 1.8% isopropanol over 40 min. The gradient was then increased to 75% 2-propanol over a period of three min., and held for ten min. to clean the column. The system was then re-equilibrated for five min. with 99:1 hexane/isopropanol. Analysis was achieved using atmospheric pressure chemical ionization–mass spectrometry (APCI–MS) using the following conditions: nebulizer pressure 65 psi, vaporizer temperature 400 ^{o}C, N_2 drying gas flow 2.5 L min.$^{-1}$, capillary voltage of 4.5 kV. Single ion monitoring (SIM) was used instead of full scanning to increase the reproducibility and signal-to-noise ratio (Schouten et al., 2007). SIM was set to scan the $[M + H]^+$ parent ion of crenarchaeol (1292) and the three $[M + H]^+$ parent ions of the branched GDGTs (1050, 1036 and 1022), with a dwell time of 200 ms for each ion. The BIT Index was calculated as follows:

$$\text{BIT Index} = (I + II + III)/(I + II + III + IV) \quad (2)$$

where, I, II, and III are the concentrations (or relative abundances) of brGDGT structures in Hopmans et al. (2004), and IV is the concentration of crenarchaeol. Recent studies (Schouten et al., 2009; Escala et al., 2009) have shown that BIT indices vary significantly among laboratories as a result of MS sensitivity differences among molecules of varying MW (i.e., terrestrial GDGTs vs. crenarchaeol). Therefore, a sample with a previously measured BIT value was analyzed daily to ensure consistency in our laboratory. The precision of repeat BIT Index measurements (%CV) was 6.7 %.

Three µL of a synthesized tetraether internal (surrogate) standard (IS) (Rethore, 2007); structure "GR") was added to the ASE extract after evaporation and before column separation. The IS has a mass of 1207.2 and is ionized during APCI analysis; therefore M/Z 1208.2 was measured in SIM mode. This IS is advantageous compared to previously used ISs (Huguet et al., 2006) as its mass is between the low terrestrial masses and high crenarchaeol mass, and also does not occur naturally. The latter allows the IS to be added before extraction and used as a measure of extraction efficiency. RRF of the IS to GDGTs in the BIT Index is not known, and therefore absolute quantities of GDGTs are not known. However, the IS can still be used to quantify the relative proportions of marine and terrestrial GDGTs as it corrects for extraction efficiency, which can vary from 20 to 90% (Huguet et al., 2010b). The ion count (IC) of each GDGT was first corrected based on the extraction and detection efficiency of the IS. The corrected IC was then normalized to the lowest GDGT response in the entire data set for the purpose of reducing the magnitude of the values, as well as the sample mass. The sample producing the lowest GDGT response in this data set was from a separate core not included in this study. The two parameters calculated this way are:

$$GDGT_{cren} = (1292_{IC} * IS_f)/(IC_{min} * g_{sample}) \quad (3)$$

$$GDGT_{soil} = ((1050_{IC} + 1036_{IC} + 1022_{IC}) * IS_f)/(IC_{min} * g_{sample}) \quad (4)$$

where, IS_f is the ratio of the IS ion count of the sample to the highest IS ion count of the entire data set, IC_{min} is the lowest ion count produced by a GDGT in the data set, g_{sample} is the mass of sediment extracted, and 1292IC, 1050IC, 1036IC, and 1022IC are the ion counts of the respective mass to charge (M/Z) ratios in SIM mode. $GDGT_{cren}$ and

$GDGT_{soil}$ therefore represent the relative abundances of crenarchaeol (marine) and branched (soil-produced) GDGTs, respectively. These parameters differ from the BIT index in that they do not reflect the absolute abundance of marine and terrestrial GDGTs to each other, but rather the absolute amount of each GDGT type normalized to sediment mass. The precision of repeat (n = 4) $GDGT_{cren}$ and $GDGT_{soil}$ measurements (%CV) was 7.7 % and 7.0 %, respectively.

Results

CuO Oxidation Products

All nine V, S, and C lignin-phenols (SAL, SON, SAD, VAL, VON, VAD, CAD, and FAD), as well as three *p*-hydroxy phenols (PAL, PON, PAD) with multiple sources were identified in this study; however not all were present in every sample. In addition to these phenols, *p*-hydroxyphenylglyoxalic acid (Pg) and syringylglyoxalic acid (Sg) were also identified (Goñi and Hedges, 1995**)**. Three fatty acid products (*n*-C_{14}FA, *n*-C_{16}FA, and *n*-C_{18}FA) were identified in a small number of sediment samples (Goñi and Hedges, 1995). BCAs identified include only 3,5 dihydrozybenzoic acid (3,5-Bd) and m-hydroxybenzoic acid (*m*-Bd) (Dickens et al., 2007). Cutin hydroxy acids and lignin-dimers were absent in all sediment samples included in the study (Goñi and Hedges, 1990; Goñi and Hedges, 1992). Due to low concentrations and low frequency of Pg, Sg, fatty acid products, and *m*-Bd, only 3,5-Bd was quantified along with the twelve V, S, C, and P phenols.

$\Sigma 8_{10}$ values ranged from 0.01 to 0.87 (0.28 +/- 0.21, n = 37) (Appendix D). The LPVI of all sediment samples ranged from 48.4 to 131, suggesting lignin-phenols were

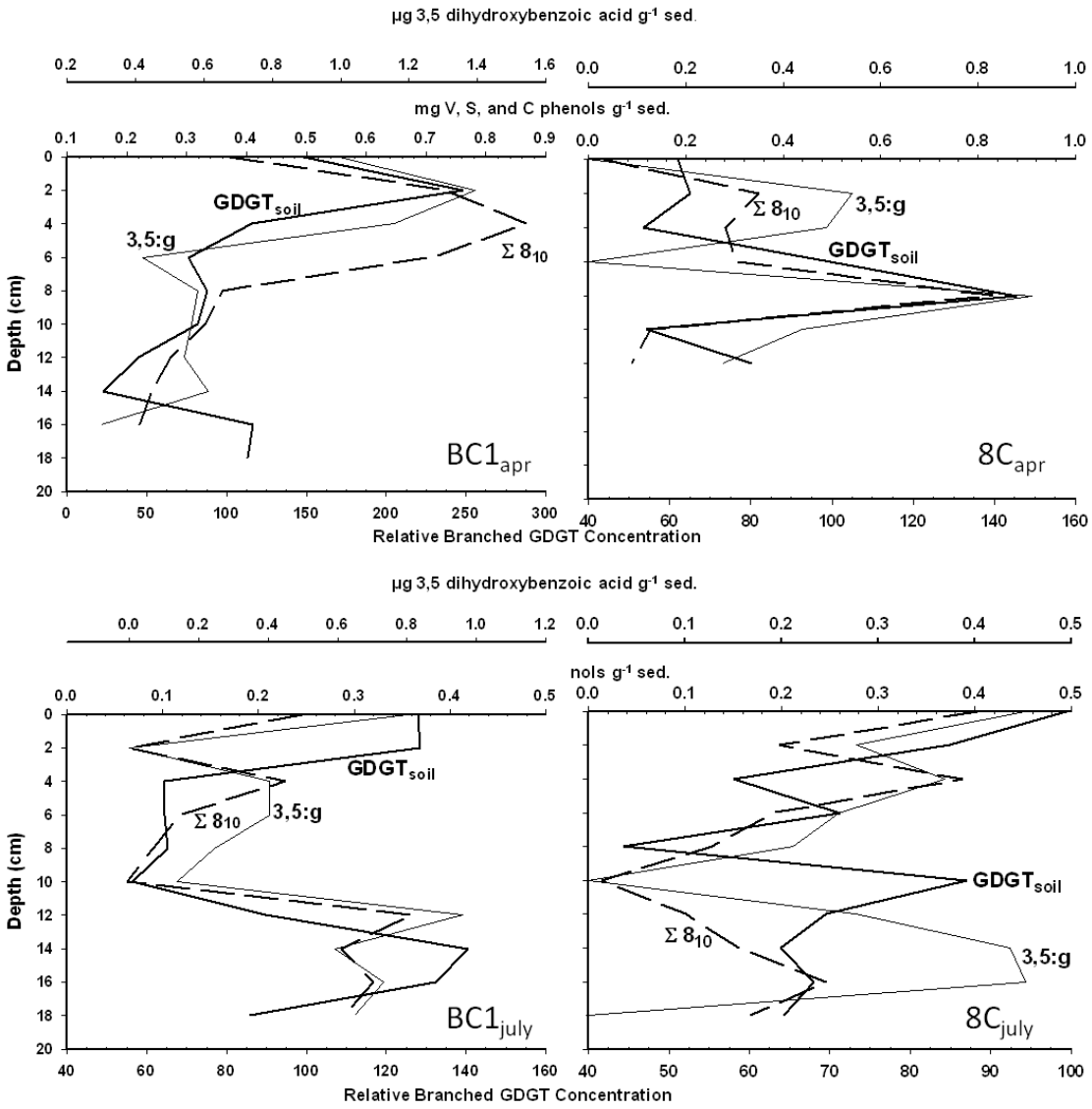

Figure 7. Lousiana Continental Shelf downcore biomarker reconstructions. Shown are sedimentary profiles of lignin (mg V, S, and C phenols g^{-1} sediment; $\Sigma 8_{10}$), 3,5-Bd (µg 3,5 dihydroxybenzoic acid g^{-1} sediment; 3,5:g), and branched GDGTs ($GDGT_{soil}$) at four locations.

produced dominantly from the oxidation of angiosperm woods, and to a lesser extent from gymnosperms (woody and non-woody) (Tareq et al., 2004). This was in agreement with other sedimentary studies in the region as well as with Mississippi River POC signatures (Bianchi et al., 2007a; Sampere et al., 2008). [Ad/Al]v values ranged from 0.17 to 0.76, indicating varying states of lignin degradation among samples. Values of 3,5:g ranged from 0.00 (below detection limit) to 1.39 μg g^{-1}.

CuO biomarkers showed no major trends with depth (Fig. 7). Lignin and 3,5-Bd concentrations fluctuate by a factor of 2 to 4, and correlated significantly in all cores (R^2 = 0.55). In core $BC1_{apr}$ (R^2 = 0.40), $\Sigma 8_{10}$ and 3,5:g remained low until ~4 to 8 cm depth (0.22-0.36 mg g^{-1} and 0.30 to 0.42 μg g^{-1}, respectively), and then spiked to 0.87 mg g^{-1} and 1.39 g g^{-1}, the highest concentrations in the dataset, before decreasing again in surface sediments. At the same location in July ($BC1_{july}$, R^2 = 0.85), both proxies had increased concentrations from 12 to 20 cm depth ($\Sigma 8_{10}$: ~0.3-0.4 mg g^{-1}, 3,5:g: ~0.6-1 μg g^{-1}), followed by a period of decreased abundance from 2 to 10 cm ($\Sigma 8_{10}$: ~0.1 mg g^{-1}, 3,5:g: ~0.1 μg g^{-1}), then elevated concentrations again at the surface. At 8C in April ($8C_{apr}$; R^2 = 0.60), $\Sigma 8_{10}$ and 3,5:g peak at 8 to 10 cm depth (0.83 mg g^{-1} and 0.91 μg g^{-1}, respectively), and exhibited a smaller peak at 2 to 4 cm depth. At the surface (0-2 cm), 3,5-Bd was below detection limits and lignin yields dropped to 0.03 mg g^{-1}. In July ($8C_{july}$; R^2 = 0.43), $\Sigma 8_{10}$ and 3,5:g peaked at 16 to 18 cm depth (0.25 mg g^{-1} and 0.45 μg g^{-1}, respectively), followed by an excursion at 10 to 12 cm where no 3,5-Bd was detected and lignin concentrations are 0.01 mg g^{-1}. Both proxies then steadily increased to 0.40 mg g^{-1} ($\Sigma 8_{10}$) and 0.45 μg g^{-1} (3,5:g) in the surface sediment.

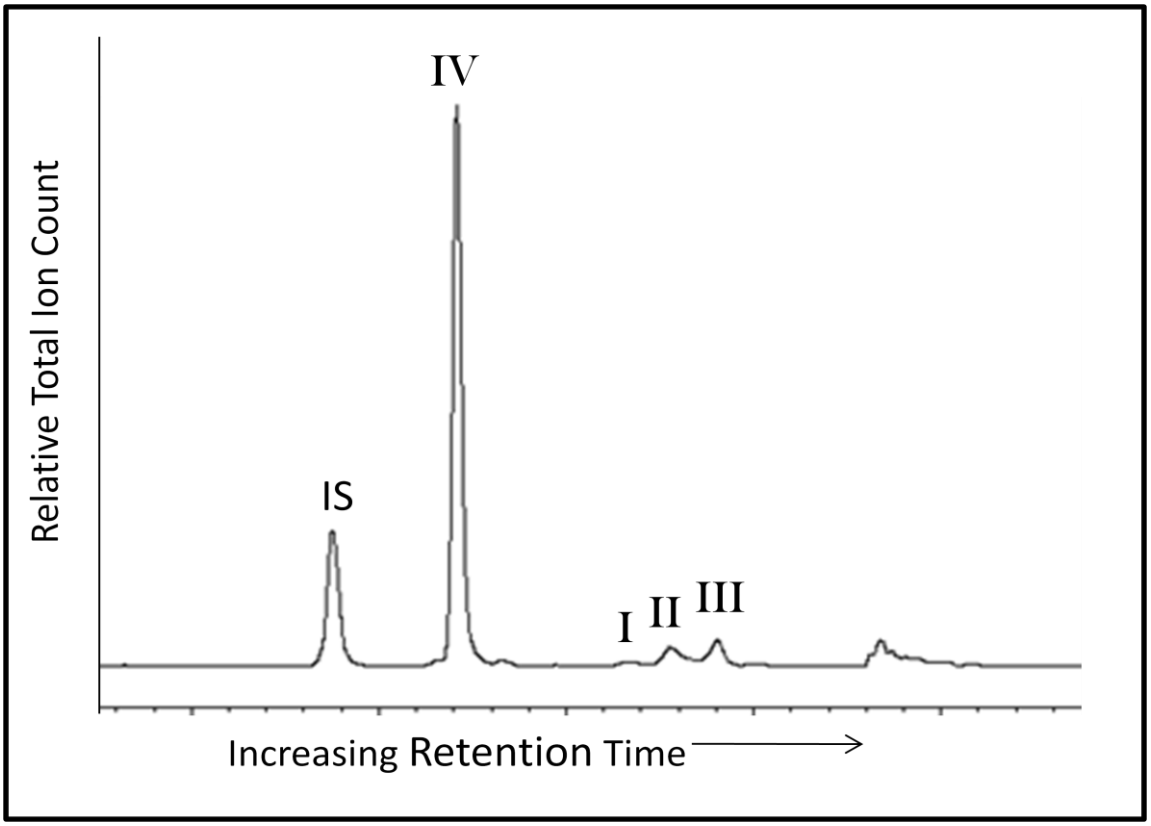

Figure 8. LC/MS chromatogram. Shown are crenarchaeol (IV), branched GDGTs (I, II, III), and the internal standard (IS; m/z: 1208.2) on SIM mode.

GDGTs

Crenarchaeol and brGDGTs I, II, and II were detected and quantified in every sediment interval, along with the IS (Fig. 8). The BIT Index in all four cores ranged from 0.50 to 0.03, within the previously measured ranges for continental shelves (Hopmans et al., 2004; Walsh et al., 2008; Kim et al., 2009a; Schmidt et al., 2010). However, the majority of continental shelf BIT values in the literature are on the low end of this

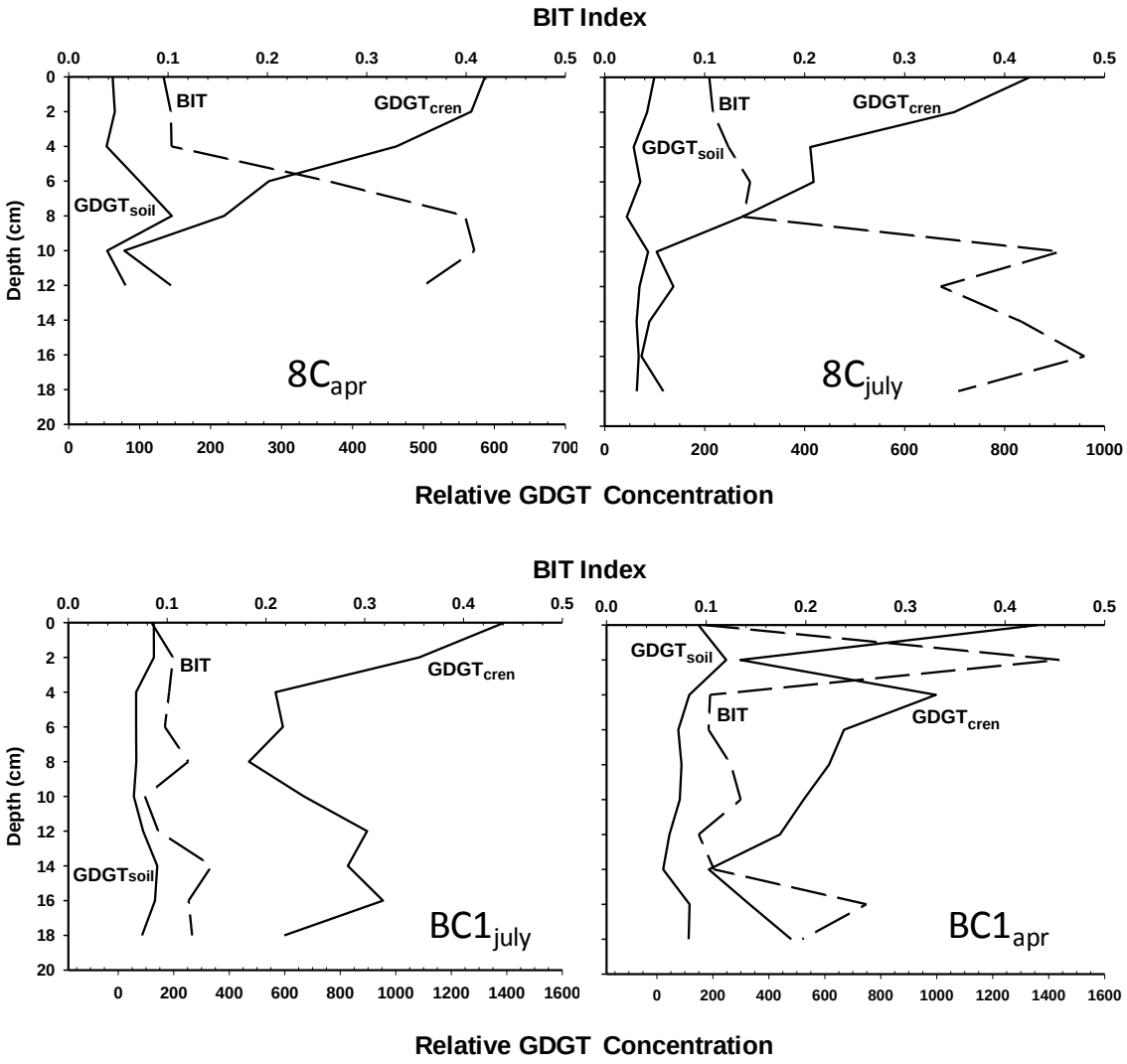

Figure 9. Sedimentary profiles of GDGT-based parameters. Shown are the BIT Index, $GDGT_{cren}$ (sediment mass normalized relative crenarchaeol concentration), and $GDGT_{soil}$ (sediment mass normalized relative branched GDGT concentration). In most cases, large changes in $GDGT_{cren}$ correspond with fluctuations in the BIT Index.

spectrum (<0.10). It was not possible to determine if there are differences in the amount of OM_{soil} delivered among regions or if the differences were largely analytical based on results from Schouten et al. (2008) and Escala et al. (2008). Although the relative magnitude of change in $GDGT_{soil}$ (CV% = 46.2, all cores) was only slightly smaller than for $GDGT_{cren}$ (CV% = 65.6%), the absolute magnitude of change of $GDGT_{cren}$ was much larger. $GDGT_{soil}$ and $GDGT_{cren}$ ranged from 22.4-248 (88.7 +/- 41.0) and 73.7-1390 (526 +/- 345), respectively, which implied higher concentrations of crenarchaeol than brGDGTs if their ionization efficiencies were similar.

While lignin and 3,5-Bd concentrations correlated strongly in all cores, the BIT Index exhibited very low correlations with either proxy. When brGDGT concentrations ($GDGT_{soil}$) were used in place of the BIT Index, R^2 values improved in all cores except for $8C_{july}$ (Appendix E). $GDGT_{soil}$ was plotted against terrestrial biomarker proxies to see if they had similar downcore trends (Fig. 9). In core $BC1_{apr}$, brGDGT concentrations were low from 6 to 16 cm along with $\Sigma 8_{10}$ and 3,5:g. $GDGT_{soil}$ peaked at the same time as 3,5:g, rather than following the slightly earlier lignin peak. In core $BC1_{july}$, brGDGTs followed the same trend as lignin and 3,5-Bd, with the exception of lower values at 12 to 14 cm and 18 to 10 cm. Additionally, the peak at the surface is deeper, down to 4 cm. In core $8C_{apr}$, $GDGT_{soil}$ peaked at 6 to 8 cm along with the other proxies, and again slightly at 2 to 4 cm. The brGDGTs did not drop as drastically in concentration at the surface as lignin or 3,5-Bd. In core $8C_{july}$, $GDGT_{soil}$ peaked at 8 to 10 cm, which was shallower than the lignin and 3,5-Bd peak. This region of disagreement explains for the

anomaly of $8C_{july}$ in Appendix E. Above 10 to 12 cm, $GDGT_{soil}$ values increased linearly with $\Sigma 8_{10}$ and 3,5:g, and peaked at the surface sediment.

All four cores have elevated $GDGT_{cren}$ values towards the surface (Fig. 9). Cores $8C_{apr}$ and $8C_{july}$ exhibit very similar trends in GDGT-based proxies. In both cores at this location, BIT Index values were high and relatively constant (~0.40) downcore from ~8 to 10 cm, and drop to ~0.10 towards the surface. The upcore decrease in BIT Index values coincided with the timing of large increases in $GDGT_{cren}$. In $8C_{apr}$, the drop in the BIT Index occurs 2 cm shallower than the onset of crenarchaeol increase due to a temporary spike in $GDGT_{soil}$. Core $BC1_{apr}$ has increasing crenarchaeol concentrations above the 14 to 16 cm interval, with the exception of a sharp decrease in $GDGT_{cren}$ at 2 to 4 cm. Values then increased again in the surface sediment. The BIT Index was slightly elevated below 14 to 16 cm, and then dropped to 0.01 corresponding with the onset of increased crenarchaeol concentrations. At 2 to 4 cm, the drop in $GDGT_{cren}$ corresponded with a large spike in the BIT Index (0.45). The BIT Index was again low in the surface sediment. In core $BC1_{july}$, BIT Index values were consistently low (~0.10) corresponding with low concentrations of brGDGTs at this site and high values of $GDGT_{cren}$. The upcore increase of $GDGT_{cren}$ at this site did not begin until 4 to 6 cm.

Discussion

Louisiana Continental Shelf Organic Matter Composition

Based on previous studies, there are two main pools of river-derived particulate OM_{terr} transported to the Louisiana Continental Shelf by the Atchafalaya and Mississippi Rivers: 1) recalcitrant OM_{soil}) associated with fine-grained minerals (clays);

and 2) waterlogged OM_{VPD} (Gordon and Goñi, 2004; Bianchi et al., 2007b). River-derived OM_{soil} associated with clays is primarily transported to deeper regions of the Gulf of Mexico and contained the residues of C_4 grasses, while much of the OM_{VPD} in this region is derived from C_3 plants from coastal forests and swamps (Goñi et al., 1997). Due to hydrodynamic sorting involving resuspension and cross-shelf transport, the denser C_3 plant detritus was concentrated in bays and on the inner shelf along with POM associated with sand and silt sized particles (Gordon and Goñi, 2004; Bianchi et al., 2007a). The composition of this OM_{VPD} may be derived from the extensive amounts of sand-sized woody materials (coffee-grinds) found in the sandy sediments in both the Atchafalaya and Mississippi Rivers - likely derived from woody plant materials (Bianchi et al., 2007a).

Low lignin and high 3,5-Bd concentrations suggest OM_{soil} was a large component of the terrestrial OC content at these sites. Additionally, significant correlations between the two proxies suggest minimal input from OM_{VPD}, which would increase $\Sigma 8_{10}$ but not 3,5:g. Terrestrial biomarker profiles at each site were variable between cores taken in April and July. The cause of this cannot be positively identified without additional analysis, but may be due to sedimentary transport mechanisms on the shelf. Lignin source and degradation parameters downcore were quite variable, and likely reflected changes in the magnitude of OM_{terr} delivered from the Mississippi River, Atchafalaya River, and associated coastal marshes (Bianchi et al., 2010; Gordon and Goñi., 2004). Since much of the aforementioned literature has focused on the transport and sedimentary dynamics of OM_{sed} along the Louisiana shelf, we have kept our

interpretation of this very brief and now focus largely on methodological considerations.

BIT Index Versus the CuO Method

The lack of correlation between the BIT Index and lignin concentration was similar to the finding of most studies involving these comparisons (Walsh et al., 2008; Belicka and Harvey, 2009; Weijers et al., 2009; Schmidt et al., 2010; Smith et al., 2010). These studies have attributed these differences to two primary explanations. The first is that the BIT Index is a measure of only the soil fraction of OM_{terr}, while lignin is derived from fresh plant matter, as well as more degraded plant material incorporated into soils (Walsh et al., 2008; Smith et al., 2010). Lignin based OM_{terr} estimates should therefore be higher than those based on the BIT Index, as is generally the case (Walsh et al., 2008; Belicka and Harvey, 2009). However, in this study, due to the strong correlation between lignin and 3,5:g, an independent proxy for OM_{soil}, OM_{VPD} was not a large component in these sediments, and cannot explain for the poor correlation between the BIT Index and lignin concentrations.

The second explanation was that large variations in crenarchaeol concentrations can control BIT Index values (Belicka and Harvey, 2009; Schmidt et al., 2010). To determine the degree to which the BIT Index in this study was controlled by variations in crenarchaeol rather than brGDGTs, R^2 values were measured in all four cores for $GDGT_{cren}$ vs. BIT Index and $GDGT_{soil}$ vs. BIT Index (Appendix F). The response of the BIT Index to changes in crenarchaeol concentrations was non-linear (due to the equation of the BIT Index), and therefore required the Log values from both sets of values. The linear regressions revealed that in all four cores, a strong relationship existed between

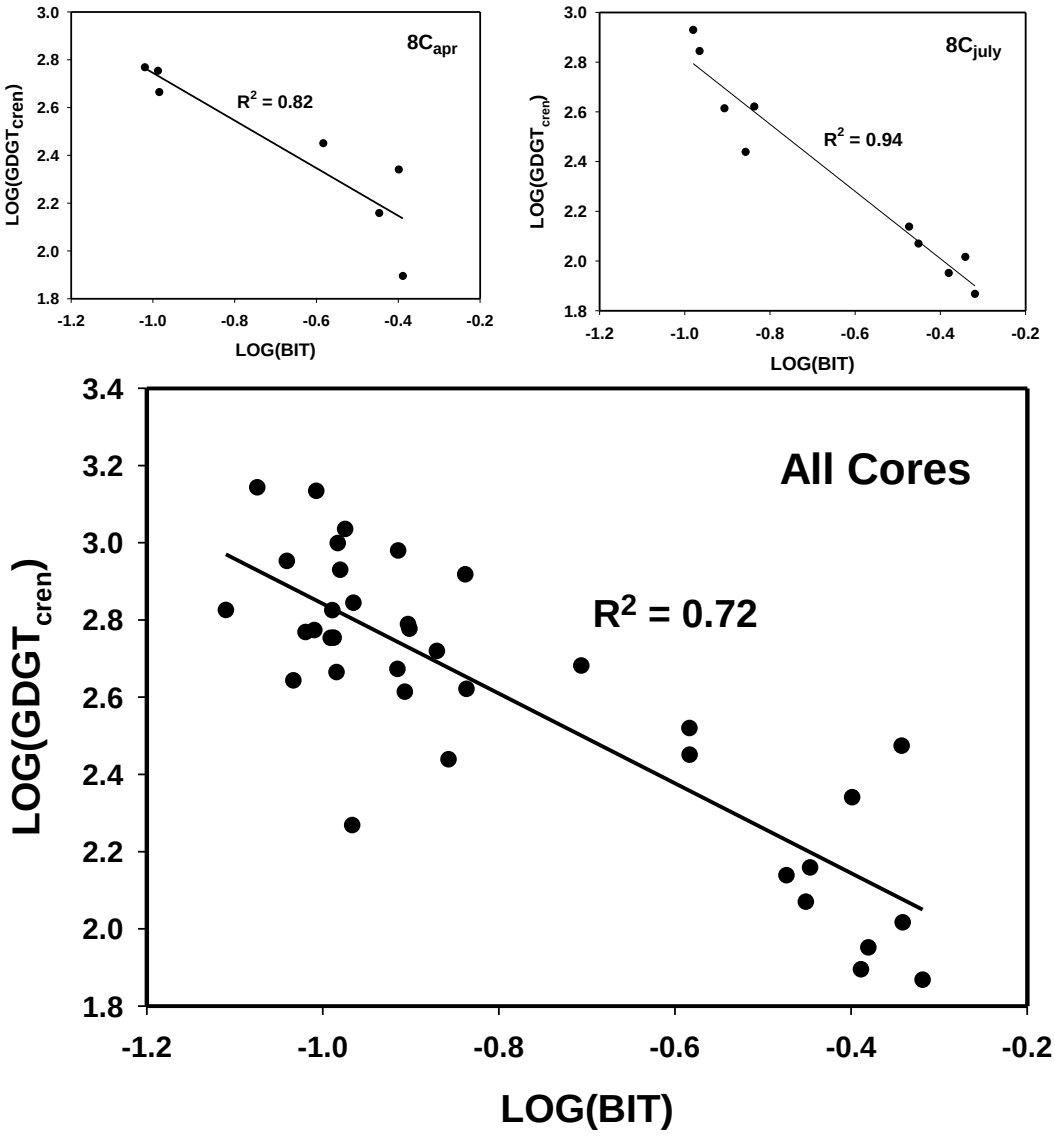

Figure 10. Linear regressions of $GDGT_{cren}$ and the BIT Index.

BIT Index values and crenarchaeol abundance (Fig. 10). When this was applied to individual cores, $8C_{apr}$ and $8C_{july}$ showed the strongest relationship between the BIT Index and crenarchaeol, while $BC1_{apr}$ and $BC1_{july}$ did not exhibit strong relationships between the BIT Index and either GDGT type. These data suggests that in two out of four cores ($8C_{apr}$ and $8C_{july}$), crenarchaeol concentrations are controlling BIT Index values. In $BC1_{apr}$ and $BC1_{july}$, BIT Index values were a function of both the amount of branched GDGTs and crenarchaeol. The compiled core data suggested that overall, on the LCS large vertical variations in crenarchaeol sedimentary concentrations were the driving force of changes in BIT Index values, as opposed to the concentration of OM_{soil}. These results have major implications for the way BIT indices have been and should be interpreted in the future.

Crenarchaeol and Linkages with Nitrogen Loading

To extend the implications of this regional study to other types of aquatic and marine environments, it was necessary to explain the large variations in crenarchaeol. Upcore increases of $GDGT_{cren}$ concentrations in all cores could be due to three possible explanations: 1) increased production of crenarchaeota and subsequent delivery to sediments over the last several decades; 2) *in situ* production of isoprenoidal GDGTs in the shallower oxygenated zone of the sediments; and 3) selective degradation of $GDGT_{cren}$ over brGDGTs.

An estimated 1.2 million metric tons of N are currently delivered to the LCS annually by the Mississippi River (Aulenbach et al., 2007) down from the peak during 1990 (Turner et al., 2007). This stimulates seasonally high levels of production on the

shelf (Justic et al., 2002). Primary production rates however are highly variable throughout the year, ranging from 0.5 g C m^{-2} d^{-1} in the winter to 10 g C m^{-2} d^{-1} in the summer, a difference of a factor of 20 (Lohrenz et al., 1990; Redalje et al., 1994; Lohrenz et al., 1999). Organic matter loading to shelf sediments over several decades has created a "memory" effect, whereby excess levels of organic carbon stimulate respiration and oxygen consumption in sediments (Rowe et al., 2002; Turner et al., 2008; Bianchi et al., 2010). This in turn causes the production and efflux of ammonia and other metabolites from sediments, which stimulates more primary production in the water column (Eldridge and Morse, 2008).

Group 1.1b marine crenarchaeota have recently been realized to play a large role in the biogeochemical cycling of nitrogen by aerobically oxidizing ammonia (nitrification) (Wuchter et al., 2006; You et al., 2009; Pitcher et al., 2010). Recent studies on continental shelves and lakes have shown that crenarchaeota GDGT concentrations in the water column follow seasonal trends in ammonia levels, generally lagging behind peaks in primary production (Wuchter et al., 2005; Damste et al., 2009). It is therefore likely that increases in nutrient loading and primary production on the Louisiana shelf over the past several decades has resulted in increased crenarchaeotal populations and fluxes of isoprenoid GDGTs to sediments. If we apply the low and high ^{210}Pb determined sedimentation rates calculated by Gordon and Goñi (2004) on the Atchafalaya Shelf (0.18 – 0.68 cm yr^{-1}) and assume constant sedimentation rates and that no large erosion or deposition events disturbed the sediment column, the increasing upcore trend of crenarchaeol at 10 cm depth at location 8C falls between the years 1952

and 1993, which coincides with the time range of increased nutrient fluxes from the Mississippi River. However, these ^{210}Pb sedimentation rates may not be applicable to our sites, as sediments in this region are often relict (Allison et al., 2000; Neill and Allison, 2005).

High levels of ammonia production in Louisiana shelf sediments may also stimulate crenarchaeotal populations *in situ*. Lipp and Hinrichs (2009) demonstrated that sedimentary archaeal communities can contribute parent GDGT molecules to the sedimentary record that degrade within relatively short periods of time into fossil molecules, thereby post-depositionally lowering the BIT Index value of the sediment. It is possible that *in situ* crenarchaeota communities have contributed to the increase in crenarcheaol in shallow sediments in this study, as they are aerobic and would proliferate more in aerated surface sediments (Lipp and Hinrichs, 2009; You et al., 2009; Pitcher et al., 2010). This could in part explain the varying terrestrial biomarker profiles but similar crenarchaeol profiles between April and July at 8C.

Finally, decreasing crenarchaeol concentrations with depth relative to branched GDGTs can be also explained by varying degradation rates. In a study of OM-rich turbidites from the Madeira Abyssal Plain, the BIT Index increased from 0.02 to 0.4 across an oxidation front due to the selective degradation of crenarchaeol in oxygenated sediments (Huguet et al., 2008). Calculated degradation rates indicated that crenarchaeol degrades twice as fast as brGDGTs. This selective degradation has been confirmed by subsequent studies (Huguet et al., 2009; Kim et al., 2009b). The mechanism for this may be the association of brGDGTs with fine-grained mineral

particles (Keil et al., 1994; Hedges and Keil, 1995; Kim et al., 2007), although some studies have shown brGDGTs and crenarchaeol to occupy the same sediment density fractions (Walsh et al., 2008 and references therein). It is unclear to what extent this process is influencing sedimentary GDGT profiles in this study, however based on sediment accumulations rates in Gordon and Goñi (2004), the timeframe of our sediment profile is shorter than in other studies that have seen sufficient degradation of GDGTs (Yamamoto and Polyak, 2009). If these sediments are in fact relict, as described in previous sections, sufficient time for selective degradation may have passed.

Without the aid of stable and radioactive isotopes (^{210}Pb, ^{137}Cs, ^{7}Be, ^{234}Th), it is unclear to what extent each of these mechanisms are responsible for the measured GDGT profiles in our study. Additionally, many of the studies involving biogeochemical cycling on the shelf have been conducted further east near the main depositional zone of the MR, and it is not clear to what extent the western Louisiana shelf demonstrates similar processes. However, these situations are likely in many types of marine environments, and therefore care must be taken in strictly interpreting the BIT Index as a OM_{soil} proxy.

GDGT-based $\%OM_{soil}$ Estimates

Previous studies have converted BIT index values to $\%OM_{soil}$ in sediments by multiplying them by 100 (Kim et al. 2006; Belicka and Harvey 2009). The equation is:

$$\%OMsoil = (I + II + III * 100) /(I + II + III + IV) \quad (5)$$

where, IV is the concentration (or relative abundance) of crenarchaeol, and I, II, and II are the concentrations of branched GDGTs as in Hopmans et al. (2004). This equation

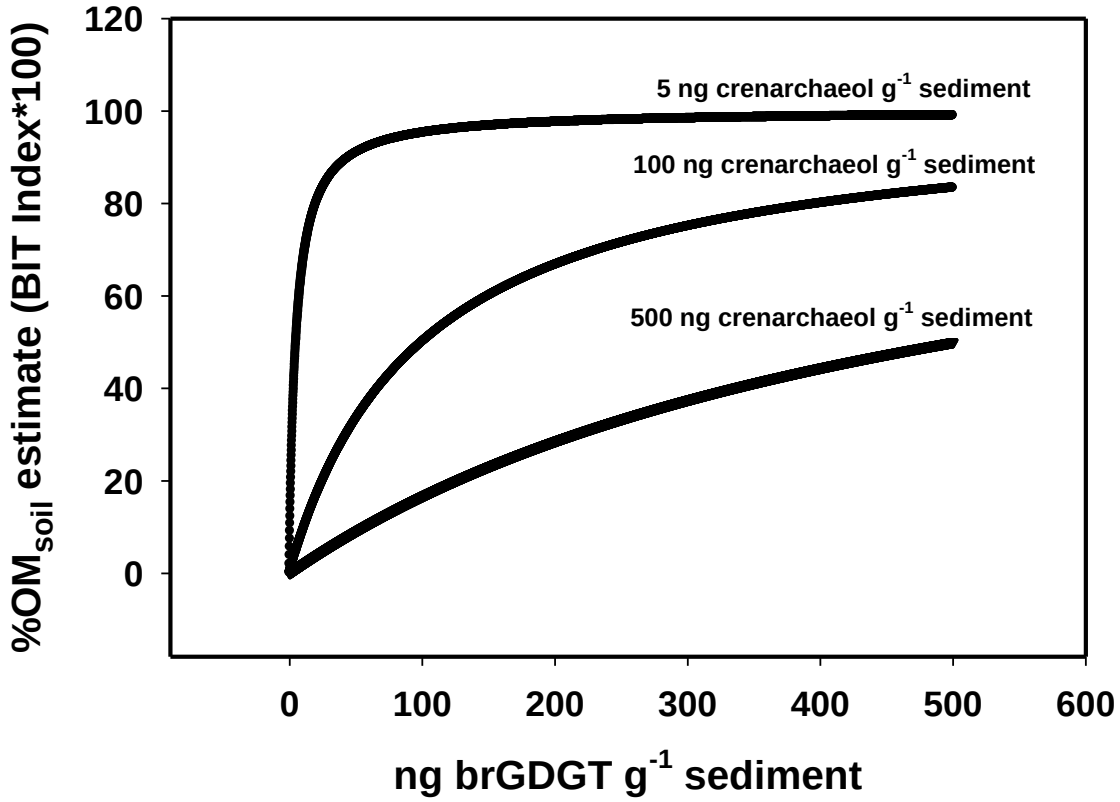

Figure 11. BIT Index-based binary mixing curves. The response of $\%OM_{soil}$ estimates in marine sediments with fixed crenarchaeol concentrations (as indicated next to each curve) to increases in brGDGT concentrations (and the BIT Index). $\%OM_{soil}$ values are calculated as BIT Index*100. The results indicate that the non-linearity of the BIT Index increases with decreasing amounts of crenarchaeol.

literally translates as the percent of total GDGTs (brGDGTs + crenarchaeol) in the sediment that were branched. The main assumption in equating this value to $\%OM_{soil}$ is that brGDGTs are a fixed proportion of the total soil organic matter pool, and crenarchaeol concentrations are fixed. The mixing line between marine and terrestrial endmembers is not linear (Fig. 11), as changes to the numerator also occur in the

denominator (I + II + III). Changes in OM_{soil} concentrations will therefore produce different magnitudes of change in the BIT Index depending on several variables, including the concentration of brGDGTs in the soil, the flux of crenarchaeol to sediments, and the range of the BIT Index values being measured. The brGDGT concentrations in soils however can range from approximately 0.1 to 300 ng g^{-1} (Weijers et al., 2006b), and their relative abundances can change as a function of both pH and mean annual air temperature (Weijers et al., 2007; Damste et al., 2008; Tierney et al., 2010). Additionally, crenarchaeota populations have been shown to vary in response to a number of factors (see section 4.3), and therefore can control BIT Index values. The effect of sedimentary crenarchaeol concentrations on $\%OM_{soil}$ estimates are demonstrated in Figure 11.

These issues can be resolved by treating brGDGTs similar to other terrestrial biomarkers. Estimates of $\%OM_{terr}$ are made using terrestrial biomarkers such as lignin and cutin by using the following two-end-member mixing model:

$$\%OM_{terr} = [([B]_{sample}-[B]_{marine})/([B]_{terrestrial}-[B]_{marine})]*100 \quad (6)$$

where, $[B]_{sample}$ is the concentration of a particular biomarker (or group of biomarkers) in the sediment sample, $[B]_{marine}$ is the marine end-member concentration, and $[B]_{terrestrial}$ is the terrestrial end-member concentration. brGDGTs are produced only in soils, so $[B]_{marine} = 0$, and the equation solves for $\%OM_{soil}$. Therefore, we suggest the following equation be used as a GDGT-based estimate for OM_{soil} abundance:

$$\%OM_{soil} = ([brGDGT]_{sample}*100)/[brGDGT]_{soil} \quad (7)$$

The terms in this equation can be substituted with either actual core-lipid brGDGT concentrations, relative values as calculated in this study ($GDGT_{cren}$ and $GDGT_{soil}$), or percent of total GDGTs as in Blaga et al. (2009). So, $[brGDGT]_{soil}$ should be calculated using the average value of as many soil samples from a watershed as possible.

In addition to being non-linear, this method overestimates the amount of OM_{soil} compared to brGDGT-based estimates using equation (7). The magnitude of this discrepancy is dependent on brGDGT concentrations in the source soils. Figure 12 examines the difference in these methods. Curve 'a' represents $\%OM_{soil}$ calculations made using equation (5). In addition to being nonlinear, the BIT-based calculation has no term for soil end-member concentrations of brGDGTs, which makes BIT Index values incomparable among study sites receiving OM_{terr} inputs from separate watersheds.

To test the magnitude of the influence equation (7) will have on previous GDGT-based estimates of $\%OM_{soil}$, we applied it to a GDGT data set from the Arctic (Belicka and Harvey 2009) that has already calculated $\%OM_{soil}$ using the BIT Index and equation (5) for comparison. The results are summarized in Appendix G. In all sediment samples but one in which there was an increase of 1.4%, equation (7) reduced estimates of $\%OM_{soil}$. On average estimates were reduced by 8.5%, and by as much as 45.1%. Station WHS-12, which had the highest magnitude of change, in particular demonstrates the accuracy of equation (7). Out of the nineteen stations included in the study, only WHS-12 had BIT-based $\%OM_{soil}$ estimates higher than the lipid biomarker based

terrestrial estimates (PCA and ALKOC). Because brGDGTs are found only in soils and lipid biomarkers are found in both soils and vascular plant detritus, estimates using the

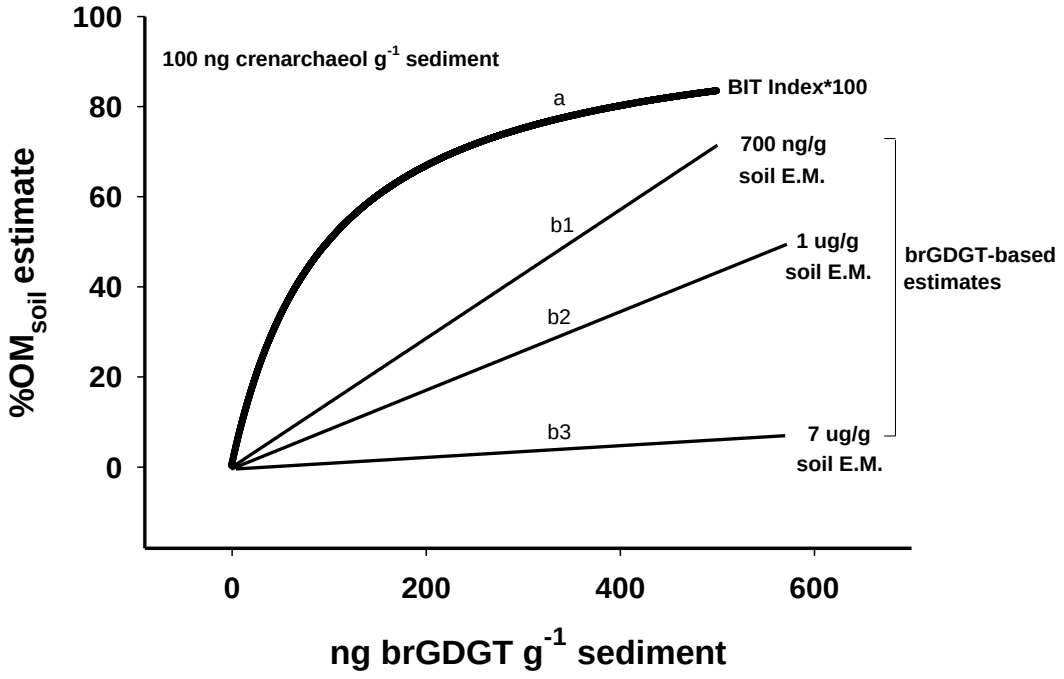

Figure 12. Modeled GDGT mixing curves of marine and terrestrial end-members. Models are generated using the BIT Index and equation (5) (curve a), as well as equation (7), the branched GDGT-based mixing model (curves b1, b2, b3), at a constant sedimentary crenarchaeol concentration of 100 ng g^{-1}. Curves b1, b2, and b3 represent source soil brGDGT concentrations of 700 ng g^{-1}, 1 ug g^{-1}, and 7 ug g^{-1}, respectively.

BIT Index ($\%OM_{soil}$) should always be lower than the biomarker based methods. Equation (7) reduced this anomalously high value and produced a BIT-based $\%OM_{soil}$ value similar to the rest of the samples in the study.

Branched GDGTs as Biomarkers

Previous studies have suggested the importance of including brGDGT concentrations along with BIT indices when determining trends in OM_{soil} deposition (Herfort et al., 2006; Kim et al., 2006). This study provides additional evidence on the utility of brGDGTs as soil biomarkers. Correlations of brGDGTs versus lignin and 3,5-Bd were stronger than correlations between the BIT Index and these biomarkers in all cores but one. Discrepancies still exist between brGDGTs and these proxies, however this is to be expected, as nearby marshes can contribute vascular plant detritus, and 3,5-dihydroxybenzoic acid can be produced by plankton (Goñi and Hedges, 1995). brGDGTs are still the only biomarkers with soil as their exclusive source, and therefore offer an opportunity to increase the resolution of organic matter fractions we can quantify in sediments to create more accurate carbon budget models.

Implications for the TEX_{86} Index

The TEX_{86} Index is a paleotemperature proxy based on the distribution of crenarchaeota produced isoprenoid lipids (Schouten et al., 2002) in sediments. Due to the presence of isoprenoidal GDGTs in soils, the presence of significant amounts of OM_{soil} in sediments can bias temperature reconstructions (Weijers et al., 2006b; Powers et al., 2010). The BIT Index is therefore commonly measured along with TEX_{86} to determine possible soil-inputs of isoprenoidal GDGTs. We suggest that while brGDGTs

are more appropriately used without reference to isoprenoidal GDGTs when quantifying soil inputs, the BIT Index is necessary to calculate in TEX_{86} temperature reconstructions. The relative bias of TEX_{86} measurements from soil inputs is based not strictly on the amount of OM_{soil} present, but also the amount of marine-derived isoprenoidal GDGTs present, which can effectively "dilute" the signal from the soil. Therefore, quantification of brGDGTs, as suggested for in OM_{soil} studies, without reference to the concentration of isoprenoid GDGTs does not provide any information on the extent to which TEX_{86} values will be biased. Powers et al. (2010) systematically applied BIT Index cutoff points, and determined that only samples with a BIT Index less than 0.50 should be included in TEX_{86} temperature reconstructions. This practice should continue use, although the cutoff point of the BIT Index will depend on the isoprenoidal and branched GDGT concentration in the source soils, which in paleoclimate studies may be difficult to determine.

Conclusion

The BIT Index was originally proposed as a proxy for OM_{terr}. These results show for the first time that crenarchaeol concentrations can control BIT Index values with no variations in the amount of OM_{soil} present. Due to the variety of factors that can control crenarchaeol concentrations in sediments, including those that directly increase the amount of crenarchaeota (ammonia concentration, seasonal stratification, *in situ* productivity) as well as diagenetic effects, this has the potential to affect terrestrial carbon reconstructions in a wide variety of marine and aquatic environments. This will be especially pronounced in large-river delta-front estuaries (Bianchi and Allison, 2009),

which have seasonal variations in nutrient inputs and stratification. Mixing between terrestrial and marine end-members of the BIT Index is non-linear, resulting in anomalously high $\%OM_{soil}$ values. The degree of non-linearity is determined by sedimentary crenarchaeol concentrations; lower concentrations produce steeper curves and higher $\%OM_{soil}$ estimates. By applying a new equation based on brGDGTs, estimates of OM_{soil} in many regions will be reduced. Use of this equation removes the bias of BIT Index $\%OM_{soil}$ estimates towards higher values, and also takes into account the concentration of brGDGTs in source soils, which is necessary in any quantitative terrestrial biomarker study. brGDGTs are soil-specific and relatively resistant to degradation, and show promise as a quantitative tracer of OM_{soil}. The BIT Index should therefore be replaced with brGDGT concentrations in future studies involving the transport of OM_{terr} to marine sediments. Finally, we propose that the BIT Index be reserved to aid in TEX_{86} temperature reconstructions.

CHAPTER IV

HISTORICAL RECONSTRUCTION OF TERRESTRIAL ORGANIC MATTER INPUTS TO NEW ZEALAND FJORDS OVER THE LAST ~500 YEARS

Introduction

Quantifying the flux of terrestrial organic matter (OM_{terr}), both soil organic matter (OM_{soil}) and vascular plant debris (OM_{VPD}), to coastal environments is critical to understanding global carbon budgets (Hedges and Oades, 1997). Changes in the size of this flux have the ability to regulate O_2 and CO_2 atmospheric budgets, as burial environments, which differ drastically between terrestrial, coastal and non-coastal marine systems, play a large role in organic matter remineralization and preservation rates (Berner and Lasaga, 1989; Burdige, 2005; Hedges and Keil, 1995; Hedges et al., 1997). Additionally, OM_{terr} generally exhibits higher preservation rates than marine-derived organic matter (OM_{mar}), as this organic matter pool is derived in-part from refractory vascular plant biomolecules such as lignin, may be mineral-associated, and has generally already been extensively processed before entry into the marine environment (Ertel and Hedges, 1985; Hedges and Keil, 1995; Keil et al., 1994).

Fjords are narrow, deep glacially carved estuaries at high latitudes formed since the last glacial maximum, and worldwide contain a greater volume of water than drowned river estuaries (Syvitski et al. 1987). They may contain over 12% of all the sedimentary organic matter (OM_{sed}) buried during the last 100,000 years (Nuwer and Keil, 2005), suggesting they are quantitatively significant burial environments when

calculating global carbon budgets. Sediments in fjords have been found to contain over 10% by weight OC (Skei 1983; Walsh et al., 2008; Smith et al. 2010), the majority which is terrestrial in origin, especially in the upstream reaches of the fjords (Nuwer and Keil, 2005; Smith et al., 2010; Walsh et al., 2008; Huguet et al., 2007; Burrell 1988). In addition its role in coastal carbon cycling, OM_{terr} is becoming increasingly realized as an important carbon source for fjord ecosystems (McLeod and Wing, 2007, Vargas et al., 2011).

Methods

Fiordland is a National Park containing 14 major fjords covering approximately 175 km of the southwestern New Zealand coastline. The physical characteristics of the fjords, along with the regional climate, result in high concentrations of OM_{sed} in fjord basins with a strong terrestrial signature (Nuwer and Keil, 2005; Smith et al., 2010). First, unlike watersheds in the North Island which have lost 40-100% of their indigenous vegetation due to anthropogenic modification, Fiordland has lost almost none (Leathwick et al., 2003). Second, Fiordland receives 6200-8000 mm yr-1 of rainfall (Sansom 1984). Third, uplift and denudation rates in the Southern alps are approximately equal, resulting in a maintained relief of 2-4 km (Hovius et al., 1997) and inclination angles of 35-65^{o} or more. Finally, the active Alpine Fault runs directly off the coast of Fiordland, making it one of the most seismically active areas of New Zealand (Hancox and Perrin, 2009). These factors result in OM_{terr} inputs to fjord sediments from; continuous leaching of organic-rich soils, large-mass wasting events of fjord slopes which deposit large areas of intact vegetation, soils, and bedrock, mountain

streams carrying over 20x the global average of POC (Lyons et al., 2002; Scott et al., 2006), and physical erosion (up to 7 mm per year) of high-grade metamorphic rocks (Bull and Cooper, 1986; Tippett and Kamp, 1993). Finally, Fiordland has been found to have some of the highest physical erosion rates in the world, and may have played a role, along with other geologically similar environments, in historical long-term CO_2 fluctuations due to weathering of OC aged on geological time scales (Hilton et al., 2008; Lyons et al., 2005).

To date, historical changes in OM_{sed} composition in southern hemisphere fjords has not, to our knowledge, been measured, despite a number of studies in Northern Hemisphere fjords (Huguet et al., 2007; Nuwer and Keil 2005, Tunnicliffe et al. 2000; Walsh et al., 2008). The handful of organic geochemical studies in southern hemisphere fjords have been restricted to the water column (Gonsior et al., 2008; Gonsior et al., 2011; Vargas et al., 2011) or surface sediments (Smith et al., 2010; Sepulveda et al., 2011; Silva et al., 2011). This study uses a dual-isotopic ($\delta^{13}C$, $\Delta^{14}C$) and multi-biomarker approach (lignin-monomers, lignin-dimers, cutin hydroxy acids) to quantify changes in the absolute amount and composition of OM_{terr} deposited to fjord basins in Fiordland, New Zealand over the last ~500 years (as determined by ^{210}Pb based linear sedimentation rates). The purpose of this study is to show that high rainfall rates and mass-wasting events in Fiordland's intact watershed create large fluxes of OM_{terr} to fjord sediments, which represents a significant organic carbon sink relative to global coastal zones.

Sample Collection

Six piston-cores (Figure 13) were collected during a 2007 cruise aboard the R/V Polaris. Cores were taken from a wide range of latitudes encompassing three fjords (Figure 13). They were stored frozen onboard the ship, and sectioned into 2 cm intervals (down to 150 cm) at the university of Otago. The sediment samples were freeze-dried and gently ground with a mortar and pestle at Texas A&M University. They were then stored frozen until analysis. Samples chosen for analysis included all 2 cm intervals down to ~500 years before present (ybp) as determined by ^{210}Pb analysis, assuming constant sedimentation rate beyond the point at which no excess ^{210}Pb is present.

Soil samples were taken using a spade with depth increments from a small craft at approximately the waterline. In all cases the leaf litter layer was cleared before the sample was taken. Samples were immediately frozen onboard, and freeze-dried and homogenized at Texas A&M. Soil samples were passed through a 500 μm sieve in order to remove large pieces of wood, roots, and leaves. S-DC1, S-DC2, and S-DC3 were taken from Deep Cove (DC) (Figure 13). S-DC1 and S-DC2 were sampled from undisturbed soil while S-DC3 was sampled from a small (several meters in width) landslide. S-GA1 and S-GA2 were sampled from Gaer Arm (GA) in a location close to the mouth of the Camelot River. S-GA1 was a surface soil sample, while S-GA2 was taken after removing the top 6" of soil. S-DS1 was a soil surface sample taken from Dusky Sound (DS), also near the mouth of a headwater stream. The two southernmost

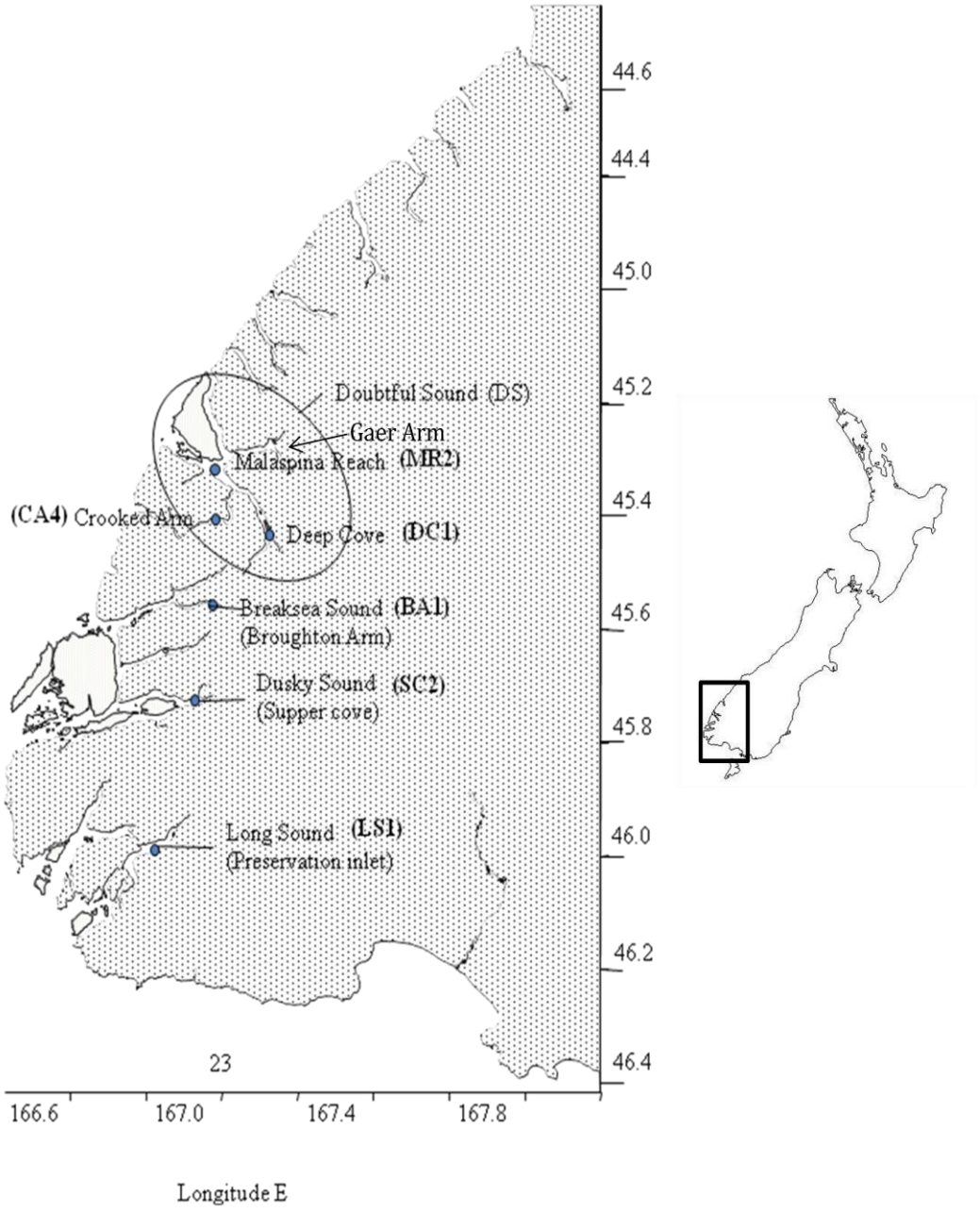

Figure 13. Fiordland, NZ sampling locations. Shown are locations of sediment cores (MR2, CA4, DC1, BA1, SC2, LS1) and soil samples (Gaer Arm (S-GA1, S-GA2), Deep Cove (S-DC1, S-DC2, S-DC3), Dusky Sound (S-DC), and Preservation Inlet (S-PI1, S-PI2)) taken from Fiordland, NZ).

soil samples (S-PI1 and S-PI2) were surface soil samples from Preservation Inlet (PI), close to the mouth of the fjord.

Vegetation samples were collected from forested areas accessible from the shoreline, and were identified at the University of Otago by C. Savage and D. Rundgren. Samples were collected to represent a wide variety of vegetation types. In the case of trees, leafs (or needles), wood, and bark were separated and analyzed separately. All samples were pulverized with a Wig-L-Bug. Peach Leaf (NIST) standards were pulverized using the same method and sent out for isotopic analysis in order to ensure no contamination from sample preparation procedure. The identity of the samples, where possible, was listed in Appendix H.

Bulk Isotope and Elemental Analysis

Total organic carbon (%OC) and stable carbon isotope analyses ($\delta^{13}C$ of sediments were carried out by the Stable Isotope Geosciences Facility (SIGF) in the Departments of Oceanography and Geology at Texas A&M University. Measurements were made using an elemental analyzer (Carlo Erba EA-1108; CE Elantech, Lakewood, NJ) interfaced with an isotope ratio mass spectrometer (Delta Plus XP, Thermo Finnigan) operating in continuous flow mode. Carbon isotope ratios were calculated in δ notation using equation (1). The precision of duplicate measurements was +/- 0.1‰. C/N values are calculated as molar ratios. N/C are also reported due the findings of Perdue and Koprivnjak (2007), which show that in a two end-member mixing model of terrestrial and marine C/N values, %N (marine or terrestrial) is actually being calculated.

%OC (marine or terrestrial) can therefore be calculated by taking the inverse of C/N values (N/C).

$\Delta^{14}C$ measurements were performed with Accelerator Mass Spectrometry (AMS) at the Woods Hole Oceanographic Institute (WHOI). Fm values were corrected for ageing to the top sediment interval (*f*mCT) in each core by using the ^{210}Pb linear-sedimentation dates and ^{14}C decay rates. (*f*mCT) values therefore represent *f*m values at the time of sediment deposition.

CuO Oxidation

Freeze-dried sediment containing 3 to 5 mg OC were analyzed for lignin monomers and dimers, and cutin hydroxy acids using the CuO method of Hedges and Ertel (1982) as modified by Goñi and Hedges (1992). Briefly, sediments were transferred to stainless steel reaction vials and digested with 330 mg (+/- 4 mg) CuO in 2N NaOH under N_2 at 150 ^{o}C for 3 h. Reaction products were allowed to cool extracted with three successive 3 ml aliquots of diethyl ether (peroxides removed with ferrous ammonium sulfate dissolved in water), dried with sodium sulfate, evaporated under a stream of N_2, reconstituted in pyridine and converted to trimethylsilyl derivatives using bis-(trimethylsilyl) trifluoroacetamide (BSTFA) at 70^{o}C for 1 hour. Oxidation products were analyzed using an Agilent 6890n gas chromatography instrument/ coupled to an Agilent 5973N mass spectrometry instrument (GC-MS).

The identification of classic lignin-phenols monomers (V,S, and C), as well as 3,5-Bd, was made by comparison with the pure standards. Cutin hydroxy acids, and lignin dimers and extended monomers were identified based on published relative

retention times and mass spectra (Dickens et al., 2007; Goñi, 1992; Goñi and Hedges, 1990; Goñi and Hedges, 1992). Compound abundances were calculated by normalizing to both mass (mg/g: Σ) and to organic carbon (OC) (mg 100 mg OC^{-1}: Λ). Quantification and % recovery of oxidation products was based on an ethyl vanillin (EVAL) surrogate standard. The relative response factors (RRFs) to EVAL for compounds with an available standard were calculated from a mixed standard analyzed with every batch of 12 samples. The mixed standard contained vanillin (VAL), acetovanillone (VON), vanillic acid (VAD), syringaldehyde (SAL), acetosyringone (SON), syringic acid (SAD), *p*-coumaric acid (CAD), ferulic acid (FAD), *p*-hydroxybenzaldehyde (PAL), *p*-hydroxyacetophenone (PON), *p*-hydroxybenzoic acid (PAD), 3,5-dihydroxybenzoic acid (3,5-Bd), 12-hydroxystearic acid (12-HSA), 16-hydroxyhexadecanoic acid (16-HHA), and hexadecanedioic acid (HDDA).

RRFs of classic lignin-phenol monomers (Hedges and Ertel, 1982) were calculated using the pure compounds in the mixed standard (VAL, VON, VAD, SAL, SON, SAD, CAD, FAD, PAL, PON, PAD), as well as the RRF of 3,5-Bd (Prahl et al., 1994), the only BCA a standard was available for. The RRFs of cutin hydroxy acids (Goñi and Hedges, 1990) were assumed to be 1, based the on RRFs of the 12-HSA, 16-HHA, and HDDA standards. The RRFs of lignin dimers and extended monomers (Goñi and Hedges, 1992) are assumed to be 1, consistent with other studies due to a lack of available standards.

Radionuclide Dating

Activities of the particle-reactive radiotracer ^{210}Pb with depth were measured using a Canberra low-energy, intrinsic germanium γ-spectrometer (well-type) to examine the timing and rates of sediment accumulation in the fjord cores. Freeze-dried sediment intervals were ground, packed in 60 mm long test tube vials, sealed to prevent ^{222}Rn loss, and allowed to grow to secular equilibrium for ^{210}Pb for at least three weeks. Samples were then counted for 1-2 days. Total activities were determined using net peak area for gamma photopeaks at 46.5 keV (^{210}Pb) and 661.6 keV (^{137}Cs). Detector efficiencies at each energy level were calibrated using a natural sediment standard (IAEA-300 Baltic Sea) and were corrected for self-absorption using the method of Cutshall et al. (1983).

Excess ^{210}Pb in the cores is calculated from total ^{210}Pb activity minus supported ^{210}Pb activities obtained using the averaged activity of ^{226}Ra daughters at 295 and 351.9 keV (^{214}Pb) and 609 keV (^{214}Bi). A best fit linear regression of the natural log of excess ^{210}Pb with depth below any surface mixed layer of homogenous activity was used to determine the sediment accumulation for the past ~100 years in the cores (Nittrouer and Sternberg, 1981). Linear sedimentation rates (LSRs) given were indicative of maximum accumulation rates.

Statistics

In the case of biomarkers where yields are given normalized to both sediment and OC mass, the Σ values are used for the statistical tests. Simple regression analyses were performed using Sigma Plot, Inc. (Version 11.0). Means are reported with a 95%

confidence interval and differences between means were established using unpaired t-tests (Sokal and Rohlf, 1995).

Results

Averaged values with more than n=2 samples were given with their standard deviations. Where two samples were been grouped together, the average was given with no standard deviation. In some cases where biomarker yields were normalized to both g sediment and 100 mg OC, the more commonly published values were used to describe trends among sample fractions.

Sedimentation Rates

Excess ^{210}Pb activities in all sediment cores were relatively low, resulting from lower than expected sediment accumulation rates, and therefore calculated dates are interpreted with caution. Sedimentation rates are assumed to be linear (LSR), and represent the maximum accumulation rate (Fig. 14). LSRs ranged from a minimum of 0.012 +/- 0.0 cm yr^{-1} at SC to 0.099 +- 0.024 cm yr^{-1} at CA.

Elemental and Isotopic Analysis

δ^{13}C values of all fresh (non-submerged) vegetation samples analyzed ranged from -27.60 to -34.91 (x = -32.01 +/- 1.86 ‰) (Appendix H). Fresh wood samples averaged -30.35 +/-.08 ‰ (n=4), while submerged wood samples were significantly more enriched in ^{13}C (-26.80 +/- 0.14 ‰, n=3). Gymnosperm wood was slightly more enriched than the angiosperm samples, although not enough samples were taken to prove significance. Bark samples were significantly more enriched (x = -33.56 +/- 1.92 ‰,

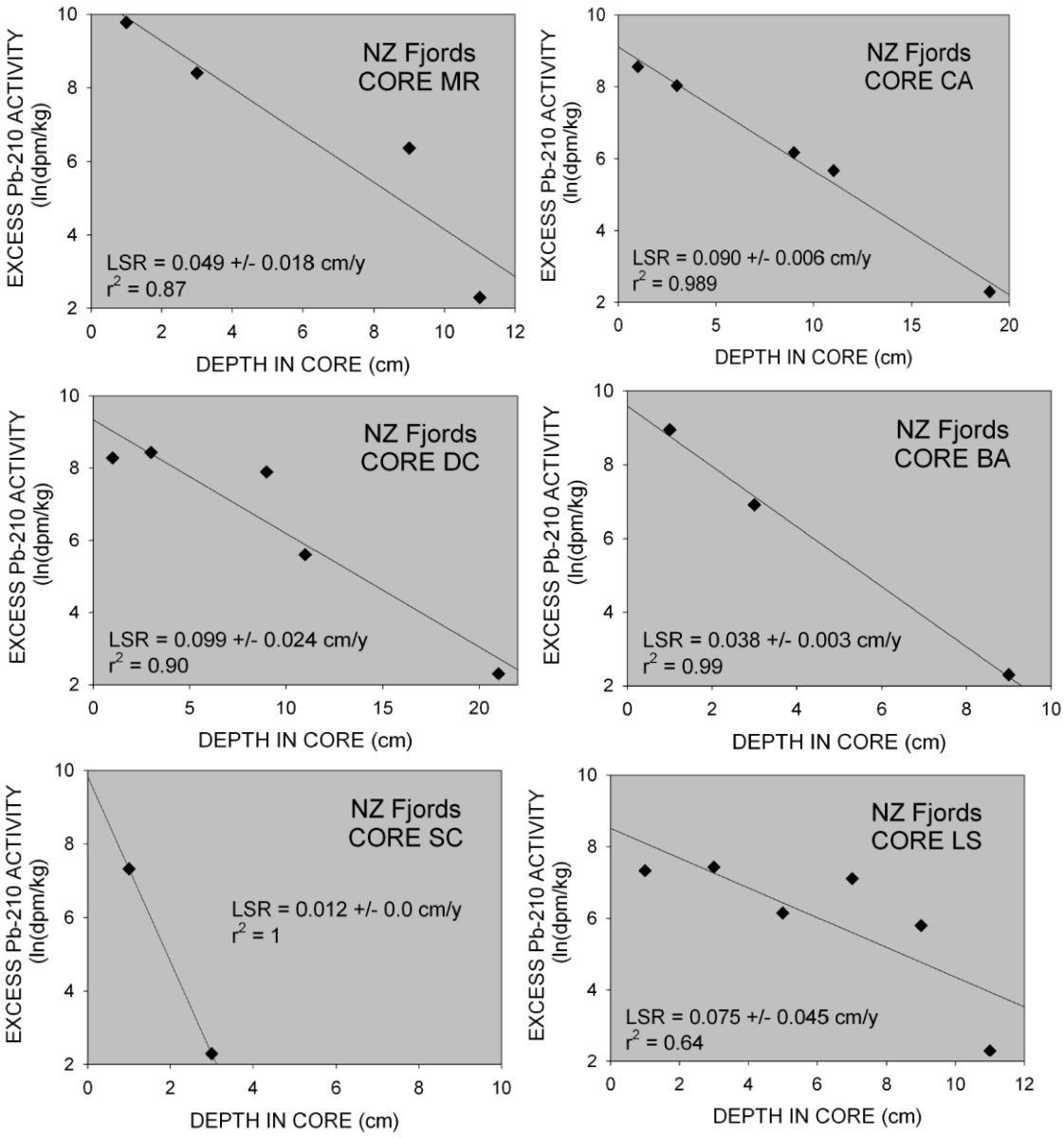

Figure 14. ^{210}Pb activities and maximum linear-sedimentation rates (LSRs).

n=2) than both wood and leaf (x = -32.74 +/- 1.16 ‰, n= 6) samples. The needle sample (33.80 ‰) had a similar value to the leaf samples. The most enriched soft-tissue sample was the marsh grass (-27.61 ‰). The unidentified epiphytes were slightly more enriched (-30.70 +/- 0.65 ‰, n=2), but similar to the mean of all vegetation samples. Soils ranged from -26.48 to -30.18 ‰ (x = -28.36 +/- 1.37 ‰, n=8). In general, soils were more enriched in ^{13}C in higher latitude fjords (Doubtful Sound vs. Dusky Sound and Preservation Inlet) (Fig. 13). In all cases, soils were more enriched than the average vegetation value. $\delta^{13}C$ values in all cores ranged from -24.29 to -28.84 ‰ (-26.84 +/- 1.18 ‰, n=76) (Appendix I). The range in values of each core was much smaller than the range among cores, as indicated by low standard deviations. CA had the most depleted $\delta^{13}C$ values (-28.0 +/- 0.51 ‰, n=17), followed by DC (-27.6 +- 0.30 ‰, n=21) and SC (-27.2 +/- 0.21 ‰, n=4). BA had $\delta^{13}C$ values in an intermediate range of all the cores (-26.5 +- 0.12 ‰, n=11), while LS (-26.0 +/- 0.28 ‰, n=12) and MR (-24.8 +/- 0.24 ‰, n=11) were the most enriched.

Soil $\Delta^{14}C$ values ranged from 70.2 to 129 ‰ (Appendix H), indicating that bomb radiocarbon had been incorporated into all soil samples and their dates can be considered post-1950. $\Delta^{14}C$ values of sediments were more depleted, ranging from -34.3 ‰ in the 2-4 cm interval of DC to -176 ‰ in the 16-18 cm interval of MR (Appendix I). When corrected for ^{14}C decay since deposition, *f*m values (*f*mCT) of sediments ranged from 0.84 to 0.98.

%OC values of pure vegetation samples ranged from 60.1 to 30.8 % (45.9 +- 6.6 %, n=22) (Appendix H). Bark samples contained the highest concentrations of OC, with

60.1% for angiosperm bark and 51.6% for gymnosperm bark. Submerged wood contained significantly lower percentages of OC (38.0 +/- 6.2 %) than fresh wood samples (47.6 +/- 1.8 %). Gymnosperm had %OC values (49.6%) slightly higher than angiosperm woods (45.5 to 48.6 %). Angiosperm soft tissue (leaves: 48.2 +/- 4.0 %) and gymnosperm soft tissue (needles: 49.9 %) values were not significantly different than both wood and the average for all vegetation samples. The two epiphyte samples had a wide range of %OC values, ranging from 31.8 % to 45.1 %. Soils contained significantly lower percentages of OC than vegetation (20.4 +/- 22.1 %), although the range was quite large (0.8 to 49.1 %). Soils overall seemed to be either depleted in OC, with concentrations less than 4%, or enriched with values similar to vegetation (42.1 to 49.1%). Only one sample (S-DC1) had an intermediate value (14.5 %). OC concentrations in sediments ranged from 1.94-11.4 % (6.1+- 2.4 %) (Appendix I). In general, ranges in each core were larger than among all six cores. Averages ranged from 8.8+/- 1.4 % (DC) to 3.7 +/- 0.2 % (MR).

Vegetation had a large range of C/N values (121 +/- 173) (Appendix H). Wood samples had the highest values, ranging from as high as 825 to 78.2, with fresh wood (274 +- 369) ratios higher than submerged wood, possibly due to the inclusion of nitrogen by submerged wood (Nuwer and Keil 2005 and references therein). Bark values were on average lower than wood (142 +- 77.4), followed by needles (112), leaves (50.6 +/- 23.5), moss (32.6) and ferns (23.5). Unlike vegetation, soils had a much smaller range of C/N values (21.8 +/- 12.1), which were lower in all cases than vegetation with the exception of Preservation Inlet soils (37.0, 44.3) which were similar

to moss, ferns, and soft-tissue. The rest of the soils were lower than vegetation, ranging from 11.8 in GA to 22.9 in DS. Sediments had C/N values statistically indistinguishable from soils (21.8 +/- 5.9), and ranged from 13.9 (MR) to 44.0 (CA) (Appendix I). CA and DC had the highest C/N values (26.9 +/- 7.5 and 24.2 +- 4.7, respectively), followed by SC (21.9 +/- 1.4), BA (19.6 +/- 0.5), LS (18.9 +/- 0.8) and MR (14.7 +/- 0.5).

Biomarkers

Lignin parameters were the highest in the submerged wood samples ($\Sigma 8$ = 78.9 +/- 18, Λ_8 = 21.1 +/- 5.4) (Appendix J), suggesting that some labile components have been degraded. For the non-submerged samples, gymnosperm wood ($\Sigma 8$ = 54.4, Λ_8 = 11.02) fell within the range of angiosperm wood ($\Sigma 8$ = 37.6 – 78.3, Λ_8 = 8.05 – 17.2). Bark ($\Sigma 8$ = 22.1 +/- 12.2, Λ_8 = 4.1 +/- 2.6) and leaf ($\Sigma 8$ = 23.1 +/- 18.5, Λ_8 = 4.6 +/- 3.5) lignin concentrations were not significantly different. Leaf samples in particular were highly variable, with $\Sigma 8$ values ranging from 5.5 to 48.4 (Λ_8 ranged from 1.2 to 9.3). Marsh grass and moss gave lower yields of lignin-phenols ($\Sigma 8$ = 13.8 and 4.2, Λ_8 = 1.3 and 3.1, respectively), followed by epiphytes which were lignin-poor ($\Sigma 8$ = 0.2, Λ_8 = 0.1). Soils varied in lignin content considerably based on location. GA soils had the lowest concentrations of lignin ($\Sigma 8$ = 0.4, Λ_8 = 1.5), followed by DC ($\Sigma 8$ = 2.7 +- 4.1, Λ_8 = 2.8 +/- 2.0). DS and PI soils had on average higher values ($\Sigma 8$ = 10.8, Λ_8 = 3.0, and $\Sigma 8$ = 21.3, Λ_8 = 5.1, respectively). $\Sigma 8$ and Λ_8 values in sediments ranged from 0.9 to 9.0 and 2.3 to 10.5, respectively (Appendix K). CA and DC had the highest lignin yields ($\Sigma 8$ = 4.9 +/- 2.5, Λ_8 = 7.3 +/- 1.8 and $\Sigma 8$ = 5.6 +/- 1.0, $\Lambda 8$ = 6.5 +/- 1.2, respectively)

followed by BA ($\Sigma 8$ = 3.8 +/- 0.8, Λ_8 = 6.8 +/- 1.0) and SC ($\Sigma 8$ = 2.5 +- 1.5, Λ_8 = 5.3 +/- 1.1). MR and LS had the lowest values ($\Sigma 8$ = 1.8 +/- 1.0, Λ_8 = 4.7 +/- 2.2 and $\Sigma 8$ = 1.3 +- 0.2, Λ_8 = 3.4 +/- 0.8, respectively).

C/V values were higher in angiosperm soft tissue (leaves = 0.20 +/- 0.17) than in both wood (submerged = 0.01 +- 0.01, non-submerged = 0.03 +/- 0.04) and gymnosperm soft tissue (0.06) (Appendix J), similar to published trends (Hedges et al., 1988). Fern non-woody tissue had a value (0.13) between wood and angiosperm soft tissue, while moss, grass, and the ephiphytes had the largest values in the dataset (0.79, 1.36, and 0.75, respectively). Soils values were dependant on location, ranging from high values in GA (0.27), to lower values in DS (0.15) and PI (0.10). DC soils ranged considerably in C/V (.09 – 0.21). Sediment values ranged from 0.04 - 0.21 (woody to soft tissue, based on vegetation end-members), with the highest values in SC (0.13 +/- 0.02) and the lowest in BA (0.05 +/- .01) (Appendix K).

S/V values also followed previously published trends (Hedges and Mann, 1979), with large differences between angiosperm and gymnosperm woods (4.07 and 0.01, respectively) and soft tissue (1.13 +/- 0.42 and 0.21, respectively) (Appendix J). Moss and Epiphytes had relatively low values (0.31 and 0.13, respectively), while marsh grass values were higher (1.47). Soils ranged from 0.27 to 0.98, with no discernable north to south trends, as GA soils ranged from 0.37 to 0.98 and PI soils from 0.62 to 0.73. Sediments ranged from a mixture of gymnosperm to pure angiosperm S/V values (0.23 to 1.88), with similar averages for all sediment cores.

[Ad/Al]v values were less than 0.30 in all vegetation samples including the submerged woods, with the exception of one epiphyte sample (0.70). Soils from GA were the most degraded (0.67), while soils from PI were the most fresh (0.28). DC (0.39 +/- 0.15) and DS (0.47) Ad/Alv values fell within this range. Sediment values ranged from 0.18 to .73, although in general the averages were indicative of fresh vegetation (range 0.23 +/- 0.03 (CA) to 0.39 +/- 0.04 (SC)) (Appendix K). [Ad/Al]s followed similar trends as [Ad/Al]v values, although they were in general lower and had a smaller range, with sediments ranging from only 0.15 to 0.37.

Yields of the extended monomer series (Goñi and Hedges, 1992), including formyl- (5f) and carboxy- (5c, 6c, 2c) lignin-phenols are given for terrestrial end-members and sediments in Appendix L and M, respectively.

3,5:V values were lower than 0.01 in all wood samples with the exception of AW-MH (0.05) (Appendix J). Bark values were higher, ranging from 0.03 to 0.08. Angiosperm leaves had low yields of 3,5-Bd with the exception of the fallen brown five-fingers leaf ($AL\text{-}FF_{FB}$ = 0.15). The needle sample was higher (0.12) than the angiosperm samples. The fern and grass sample were also low (0.02 and <.01, respectively), and the moss (0.16) and epiphyte samples (1.5, 5.7) contained elevated concentrations of 3,5-Bd. Soils, as expected, had higher 3,5:V values, ranging from 0.04 to 0.17 (0.11 +/- 0.04), than fresh soft and woody tissue (Prahl et al., 1994). Sedimentary 3,5:V were surprisingly lower than soils (0.05 +/- 0.01), indicating they are probably a mix of soils and fresh plant material (Appendix K). The averages among all cores were similar, with the lowest at BA (0.04 +/- 0.01) and the highest at SC (0.07 +/-

0.00). Yields normalized to sediment mass (Σ3,5:g) for terrestrial end-members and sediments are given in Tables 10 and 11, respectively.

Dimer concentrations (ΛD) were the highest in the submerged wood samples (4.4 +/- 2.4), followed by non-submerged wood (2.3 +/- 1.5) (Appendix N). Bark had very similar yields as wood (2.4). Soft tissue gave lower yields of dimers, both leafs (0.5 +/- 0.3) and needles (0.8). Moss and grass gave the lowest yields (0.1 and 0.2, respectively), while epiphytes were under the limit of detection. Soil values ranged from 0.2 to 1.6, with the lowest yields from GA (0.4, 0.63) and the highest from PI (1.2, 1.6). Sediment samples had ΛD values ranging from 0 to 2.02 (Appendix O). The lowest averages were from LS (0.5 +/- 0.1) and the highest from CA (1.2 +/- 0.6). Concentrations of dimer classes, as well as dimer-based proxies, are given in Appendix N and O.

Cutin hydroxy acid yields normalized to OC (ΛC_A) in fresh plant material were the highest, although highly variable, in leaves (6.7 +/- 5.05) followed by needles (3.9), bark (2.4), and wood (1.4 +/- 2.1) (Appendix P). The individual sample with the highest yield of cutin oxidation products was AL-FF_{FB} (12.0), suggesting selective degradation of more labile components. The fern, moss, epiphyte, and grass samples gave very low yields (< 0.6). Soil samples varied considerably, with the lowest cutin concentrations in DC (0.9 +/- 0.1) and the highest in DS (17.8). Cutin yields of sediments ranged from 0.0 to 6.0 (Appendix Q). MR had the lowest average yields (1.0 +/- 0.4) while CA (2.5 +/- 1.5) and DC (2.7 +/- 1.2) gave the highest. Cutin hydroxy acid yields normalized to sediment mass (ΣC_A) were much more variable in pure vegetation, ranging from 0.2 to 20.5 in woody material, 6.5 to 20.7 in bark, and 1.7 to 62.3 in leafs. S-DS was enriched

similar to the OC normalized values (72.5), and sediments ranged from 0 to 4.25. In most cases, the yield of C16 hydroxy acids was higher than C18.

Discussion

OM_{terr} Composition

Detailed compositional information of soils and sediments was obtained using source plots of several classes of CuO biomarkers and values of New Zealand angiosperm and gymnosperm vegetation. Vegetation end-members were separated into angiosperm wood (A), angiosperm leaves (a), gymnosperm wood (G), and gymnosperm needles (g). In the classic lignin monomer source plot (Fig. 15), fern values were also given, and gymnosperm and angiosperm woods fell within the same range and were labeled as wood (W). Actual points for vegetation were not shown, only the range of values as indicated by boxes; however the ranges as well as the actual values for soils were shown in order to distinguish differences between samples collected at various locations. The advantage of this data set was the use of vegetation from the study region, as opposed to Smith et al. (2010) in which traditional end-member values were used (Hedges and Mann, 1979).

Syringyl phenols are produced in much higher quantities from the oxidation of angiosperm tissue as opposed to gymnosperm tissue, while cinnamyl phenols are produced in significant quantities only in soft-tissue (Hedges and Mann, 1979). The vegetation analyzed in this study produced a very similar source plot as in Hedges and Mann, (1979), with the exception of angiosperm woody and non-woody tissue which had S/V values as low as 0.5, as opposed to ~1 (Fig. 15). Soil values overlapped only

with angiosperm soft-tissue, indicating this as the dominant source of OM. The majority of sediment samples fell into the overlapping range of woody and non-woody angiosperm tissue, although cores DC and LS ranged from the overlapping area to the box representing only angiosperm soft-tissue, closer to the range of soils. These results

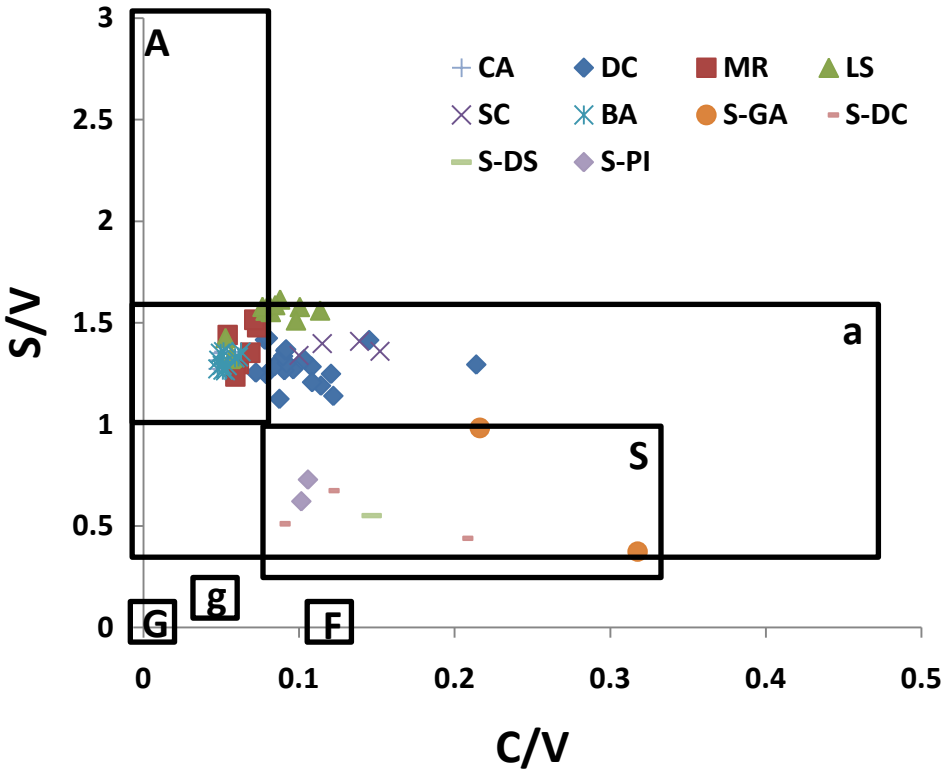

Figure 15. Lignin-phenol source plot as in Hedges and Mann (1979). A = angiosperm wood; a = angiosperm leaves; G = gymnosperm wood; g = gymnosperm needles; F = ferns; S = soils. Shown are values for soils and sediments.

indicated woody material is not incorporated in large amounts into soils, but does in fact make it into sediments. The most likely physical method for this is landslides, which uproot trees, break them up, and deposit them into the fjords. Soft-tissue on the other hand is incorporated efficiently into soils from falling leaves, as soils noticeably contain a top layer of leaf litter that had to be cleared before taking samples.

Dimers are present in both woody and non-woody angiosperm and gymnosperm tissue (Goñi and Hedges, 1992) and therefore can also be used to distinguish between these sources. Lignin-dimers provide lignin structural information that can not be obtained from the quantification of monomers alone. In many cases the structure of lignin is related to the relative yields of S, V, and C monomers, as additional functional groups prevent bonding of the ring structures (Goñi and Hedges, 1992). Structural information can be viewed as the the ratio of dimers with side-chain to ring bonds (SR; $\beta1$, $\alpha1$, $\alpha5$, and $\alpha2$ dimers) versus dimers with ring to ring bonds (RR; 55'VV and 55'PV dimers) (SR/RR), or as the ratio of C1-linked structures to dimers linked at the C5 and C2 aromatic carbons $(\beta1 + \alpha1)/(\alpha5 + \alpha2)$ (Goñi and Hedges, 1992). Goñi and Hedges (1992) found SR/RR and $(\beta1 + \alpha1)/(\alpha5 + \alpha2)$ values were elevated in angiosperm tissue, due to increased occurrence of syringyl phenols which cannot form bonds on C5 ring carbons. Gymnosperm wood was found to consist of primarily 5,5'-RR bonds and similar amounts of C1, and C5- and C2- linked structures $((\beta1 + \alpha1)/(\alpha5 + \alpha2)$ approximately = 1). Fiordland vegetation fell into different ranges of values than the vegetation analyzed in Goñi and Hedges (1992), highlighting the importance of using location-specific end-members (Fig. 16). Angiosperm leaves had similar ($\beta1$ +

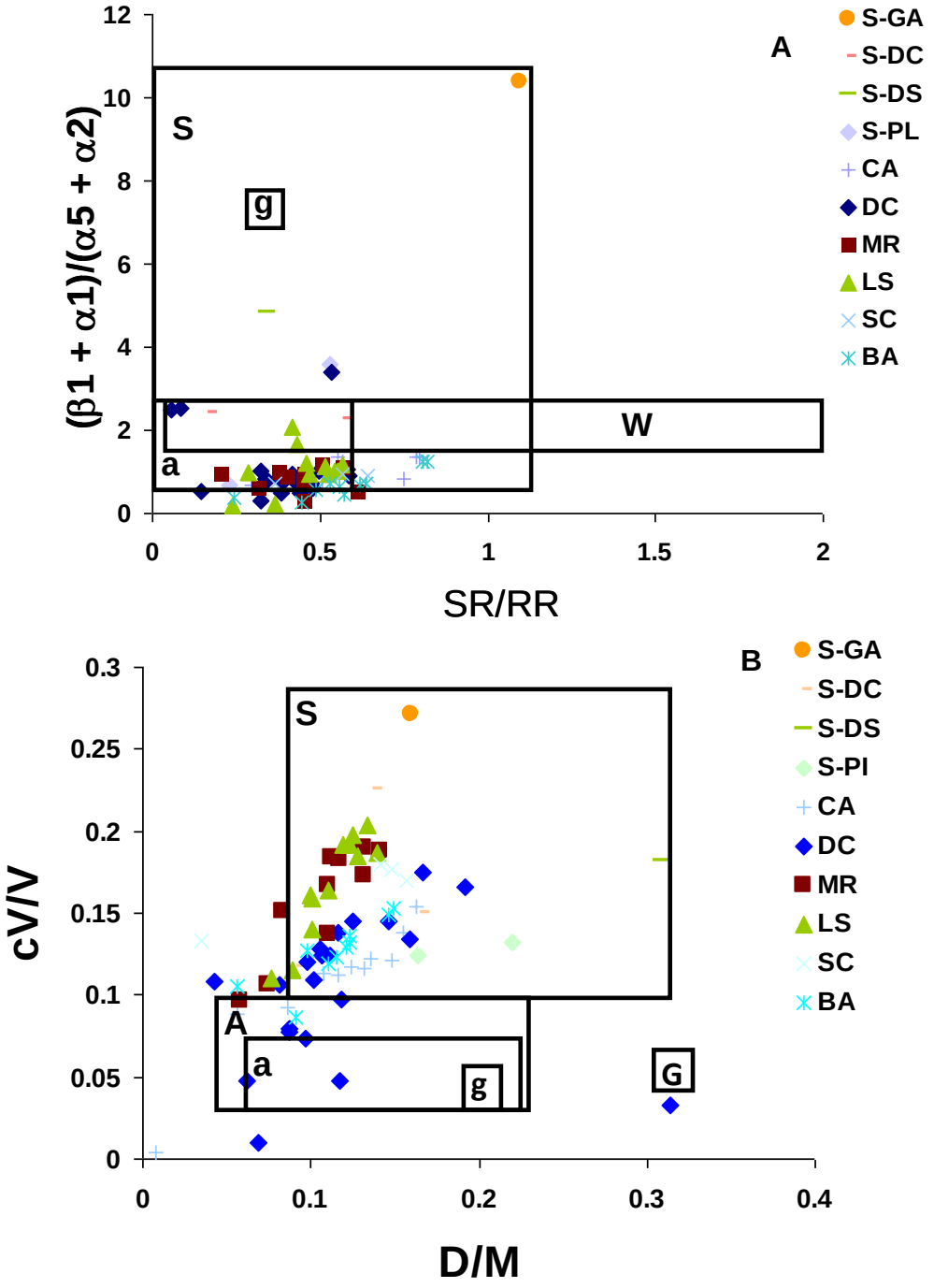

Figure 16. Lignin-dimer source plots as in Goñi and Hedges (1992). A = angiosperm wood; a = angiosperm leaves; G = gymnosperm wood; g = gymnosperm needles; W = angiosperm and gymnosperm wood. Shown are soils and sediments.

$\alpha 1)/(\alpha 5 + \alpha 2)$ values but were more depleted in SR linkages. The gymnosperm sample had a similar SR/RR value, but was many times more enriched in C1-linkages, having the highest value of all the vegetation in this study and in Goñi and Hedges (1992). Soils cover a large range on the source plot. Most of the sediments plotted on the region where angiosperm soft-tissue, wood, and soils overlap. However, most of the soils had higher $(\beta 1 + \alpha 1)/(\alpha 5 + \alpha 2)$ values, and the soil source box overlaps with angiosperm soft tissue due to only one PI sample. Therefore, as indicated in the S, V, and C source plot, most sediments contain OM_{soil} but also variable inputs of fresh woody and non-woody angiosperm material.

The extended suite of lignin monomers in Goñi and Hedges (1992) allowed additional source distinctions to be made. The ratio of dimer to total monomer yields (D/M), has been found to be generally low in angiosperm wood and higher in soft-tissues (Goñi and Hedges, 1992). These values were plotted against cV/V ratios and shown in Fig. 16. Angiosperm woody and non-woody tissue overlapped but had lower relative yields of cV monomers than soils. Sediments had values of cV/V and D/M that were positively linearly correlated in all of the cores. Sediments ranged from approximately the center of the soil range, towards angiosperm leaf and wood values. This also was in accordance with the findings of other lignin-based source plots in this study, with the linear mixing of soils and fresh vegetation providing additional robust evidence for incorporation of discrete vascular plant material into sediments.

Cutin yields were either under the limit of detection or extremely low in woody samples. Additionally, many of the vegetation types separated using other biomarkers

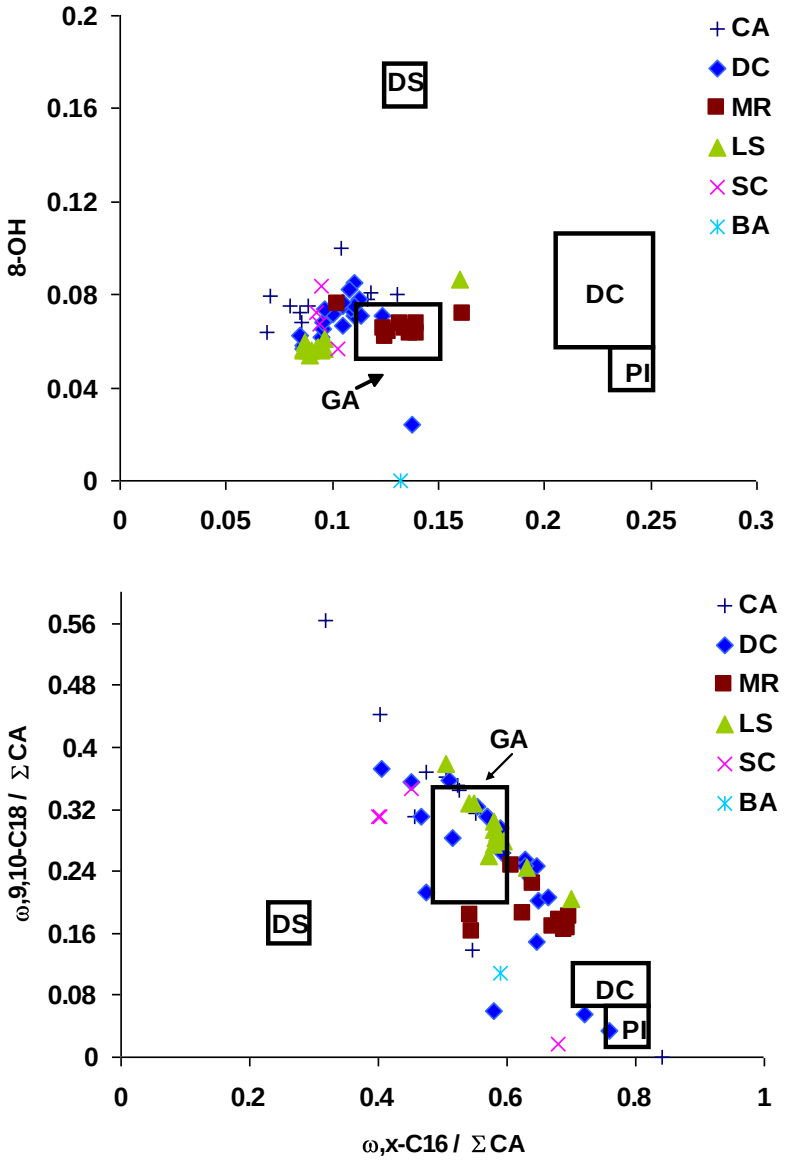

Figure 17. Cutin hydroxy acid source plot as in Goñi and Hedges (1990). Boxes represent ranges of values in soil samples. Plotted are sediment values.

overlapped when constructing source plots found in Goñi and Hedges (1990b). However, cutin yields revealed distinct differences among our soil samples, and this was instead used to show relationships between sediments and soil location. The first parameter observed was the relative abundance of positional isomers (9-OH vs 8-OH) of the x,ω-C16 hydroxy acids (Fig. 17). All values are less than 0.3, as the 10-OH isomer was the dominant hydroxy acid. GA, DC, and PI soils had similar 8-OH fractions (~0.08), with varying fractions of 9-OH isomers. DS soils had a similar 9-OH fraction as GA soils but a higher fraction of 8-OH, which was the highest of all soils in the dataset. Interestingly, all sediments plotted closest to GA soil values. MR sediment values in particular, with the exception of two sediment fractions, fell entirely into the range of GA soil values. No linear trends were seen as in lignin monomer and dimer source plots (Figs. 15 and 16), indicating no clear mixing of two sources with varying isomer fractions. Similar results were obtained comparing the relative amounts of ω,9,10-C_{18} and ω,x-C_{16} hydroxy acids to total cutin yields (ω,9,10-$C_{18}/\Sigma C_A$ and w,x-$C_{16}/\Sigma C_A$, respectively) (Fig. 17). These parameters were used in Goñi et al. (1990b) to distinguish between lower and higher vascular plants, as well as monocots, gymnosperms, and dicots. DC and PI soils fell nearly into the same range on the plot, with DC soils having slightly higher amounts of ω,9,10 hydroxy acids. DS soils had higher yields of this fraction, but significantly lower yields of ω,x-C_{16} hydroxy acids than the other soils. GA soils gave the highest yields of ω,9,10-C_{18} hydroxy acids and intermediate yields of ω,x-C16. As in the previous cutin plot, sediment samples fell predominantly near or within the range of GA soils. However, a major difference in this

source plot is the linearity of 2,9,10 and ω,x-C_{16} values, indicating mixing of two end-members, potentially OM_{terr} delivered by overland runoff and landslides.

$\delta^{13}C_{mar}$

Regressions of biomarker yields vs. $\delta^{13}C$ have been previously used in the literature to obtain an estimate of the $\delta^{13}C$ value of pure marine organic matter ($\delta^{13}C_{mar}$) (Goñi et al., 2000; Prahl et al., 1994). This method is used due to the wide range of $\delta^{13}C$ values found among species of algae and plankton, complicating measuring an average $\delta^{13}C_{mar}$ value directly. Additionally, variations in the levels of shading (irradiance) in Fiordland due to topography and fjord width may cause regional changes in $\delta^{13}C_{mar}$ values based on the availability of dissolved CO_2 (Kubler and Raven, 1995). To determine the usefulness of this method to our dataset, regressions were calculated as the OC normalized yields (Λ; mg/100mg OC) of the main terrestrial CuO biomarker classes (V,S, and C monomers (Λ_8), dimers (Λ_D), cutin hydroxy acids (Λ_C)) vs. $\delta^{13}C$ values (Fig. 18).

In all three cases the regressions resulted in weak, but significant correlations ($p < 0.05$ in all cases) that intercept the x-axis at $\delta^{13}C_{mar}$ values ranging from -23.62 to -21.66 ‰ (-22.83 +/- 1.03 ‰, n=3) (Fig. 18). This technique however is sensitive to the choice of samples to include in the regression (Goñi et al., 2000). Sediments with $\delta^{13}C$ values similar to terrestrial vegetation and soils may have wide ranges of biomarker yields, as pure terrestrial matter exhibits these large variations. By applying a cutoff point of -28 ‰ based on values of terrestrial end-members which were more depleted

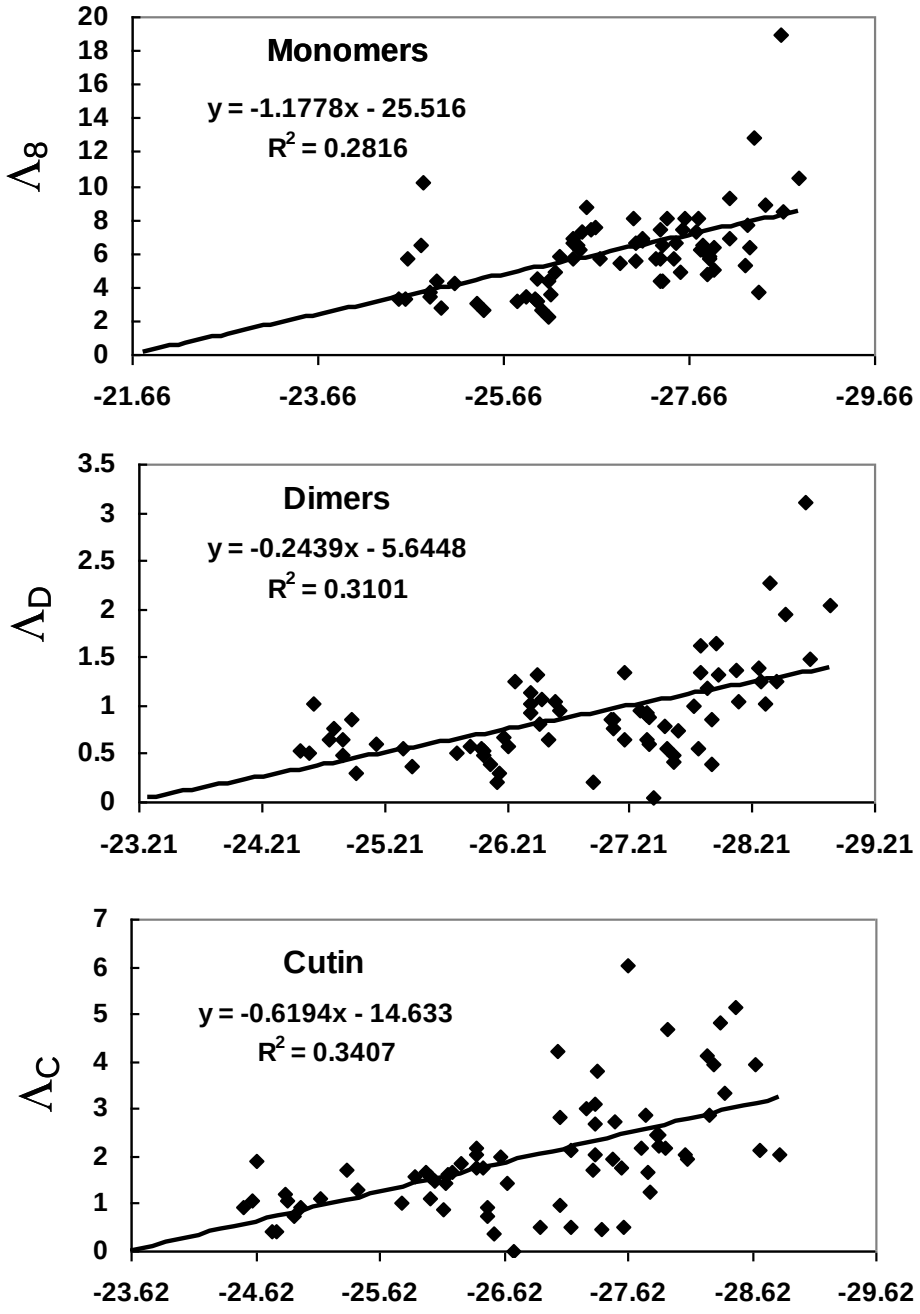

Figure 18. Linear least squares biomarker regressions.

than this value, we recalculated the x-axis intercept and measured $\delta^{13}C_{mar}$ values of -19.36 ‰ (monomers), -23.13 ‰ (cutin), and -19.65 ‰ (dimers), resulting in an average $\delta^{13}C_{mar}$ value of -20.71 +/- 2.09 ‰ (n=3). The associated R^2 values dropped (R^2 = 0.200, 0.231, and 0.100 respectively), while still retaining their significance. An unpaired t-test (two-tailed) showed that this new intercept is significantly different ($p < 0.0001$) than the previous estimate including all the sedimentary data. The regressions in Goñi et al. (2000) did not have lower R^2 values, as shown here, when samples with large yields of terrestrial biomarkers were excluded. While the correlations are weakened, the estimated δ^{13}Cmar value seems more realistic, as the value is in between that of SPOM and macroalgae (McLeod and Wing, 2007), and therefore these intercepts will be used from this point on.

The average intercept of all three regressions (-20.71 +/- 2.09 ‰; $\delta^{13}C>-28$ ‰) should theoretically equal the $\delta^{13}C$ value of OM_{mar}. Suspended particulate organic matter (SPOM) analyzed by McLeod and Wing (2007) had a more depleted $\delta^{13}C$ value (-23.5 ‰) than the estimated $\delta^{13}C_{mar}$ values given here, likely due to a significant fraction of OMterr present in the samples. However, Susanne and Schuller (unpublished data) gave a value of ~-23.5 ‰ for a phytoplankton bloom, suggesting that the SPOM may actually contain a negligible amount of OM_{terr} relative to OM_{mar}. A $\delta^{13}C$ value of -18% was obtained by Mcleod and Wing (2007) as a biomass weighted average of four genera of macroalgae that comprise 90 % of the population in the LSL (*Ulva* sp., *Gracilaria* sp., *Gymnogongrus* sp., and *Cladophora* sp.), a value which is several per mil more enriched than the value at which no recognizable terrestrial biomarkers are present.

Despite the potential of $\delta^{13}C_{mar}$ variations with topographic shading, out dataset was not sufficient to determine these differences, which should be examined in future studies.

$\delta^{13}C_{terr}$

The terrestrial end-member varied between soils and vegetation, as well as among plant tissue and type (-26.64 to -34.91 ‰). Averaging all the measured values for soil and vegetation could potentially cause a bias in estimating the true $\delta^{13}C_{terr}$ value, as it would not reflect the real weighted average that would be based on the relative amounts of soil vs. vegetation input, as well as the relative abundance of plant tissues and types in the watershed. An alternative is to use the average $\delta^{13}C$ value of soils (-28.42 ‰), and assume they reflect weighted averages of local vegetation $\delta^{13}C$ values, which is the main source of their carbon. However, averaging the soil $\delta^{13}C$ values to obtain a terrestrial end-member also creates a bias as we observed changes in the OC signature of the soils based on sampling location. It was therefore necessary to take a detailed look at the soil samples obtained and see if unique $\delta^{13}C_{terr}$ end-member values needed to be assigned to sediments based on location.

GA soils, the Northernmost soil samples taken, were the most enriched in ^{13}C (-26.5 and -26.9 ‰) and had correspondingly low C/N values and concentrations of lignin and 3,5-Bd (Fig. 19). Additionally, GA soils had distinct values from other soils in lignin monomer and dimer source plots (Figs. 15 and 16). DC soils spanned the largest range of 13C values, from -27.1 to -28.8 ‰, which were significantly more depleted than GA soils, but also had low C/N values and terrestrial biomarker concentrations, with the exception of S-DC2 which was significantly more enriched in

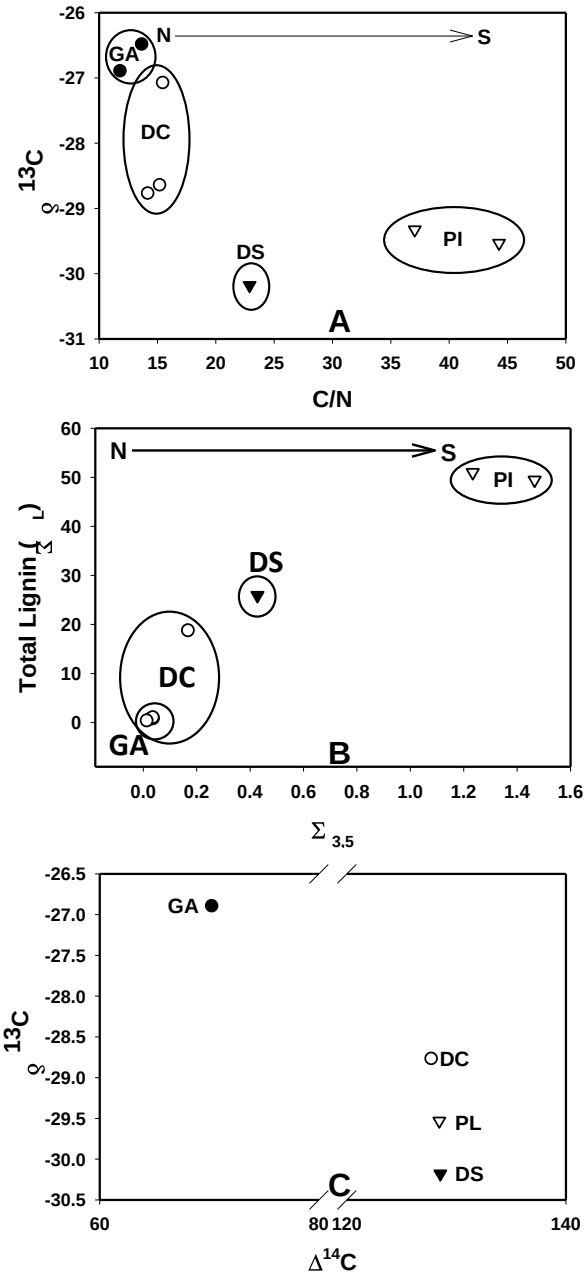

Figure 19. Bulk and biomarker soil composition of samples from Gaer Arm (GA), Deep Cove (DC), Dusky Sound (DS), and Preservation Inlet (PI). A) $\delta^{13}C$ vs. C/N, B) ΣL vs. Σ3,5-Bd, C) $\delta^{13}C$ vs. $\Delta^{14}C$.

lignin. The DS soil sample was the most depleted in ^{13}C (-30.2 ‰) and had higher C/N, ΣL, and Σ3,5-Bd values than both GA and DC. PI soil ^{13}C were similarly more depleted than GA and DC, and these soil samples contained the highest terrestrial biomarker concentrations and had the highest C/N values.

These results suggest that there are distinct differences in soil type that seemed to follow a general North to South trend. The most apparent physical North to South trend in the watershed of Fiordland is a reduction in topographical height and slope gradients. This topographical trend also results in a reduction in the frequency of landslides the more southern fjords experience. There are therefore two potential source variations that could cause the observed soil trends, both themselves a function of landslide frequency; 1) variations in soil maturity and forest composition (successional stage), and 2) dilution of organic-rich soils with organic-poor minerals.

Potential vegetational changes feeding soils were observed with lignin monomer and dimer source plots. All of the soils plotted in the same region of the S, V, and C source plot (Fig. 15), with the expection of GA, which was significantly more enriched in both syringyl and cinnamyl phenols. The values of GA gravitated towards those of angiosperm soft-tissue. If the relative monomer yields are due to differences in vegetation, the terrestrial end-member data set is not sufficient enough to distinguish them. It is possible that soils in GA are fresher than soils to the south, due to increased landslide frequency, and the higher S/V and C/V values reflect non-degraded lignin, which would reduce S and C phenols preferentially to V phenols (Opsahl and Benner, 1995). Soils in GA however in fact had higher Ad/Al ratios (~0.6), and soils to the south

were much fresher (Appendix J). It was therefore likely that the compositional differences of monomers are due to variations in the relative abundance of vegetation types on slopes facing the fjord.

The addition of mineral-rich organic-poor sediments (sourced from weathered sedimentary bedrock) was assessed with $\Delta^{14}C$ values. All of the soils had modern $\Delta^{14}C$ signatures that were not significantly different except for GA, which had a more depleted, but still modern, value (Fig. 19). It is therefore likely that GA soils have more OM_{fossil} due to mechanical weathering of sedimentary bedrock from landslide activity. Without separation of the two fractions (organic soils and weathered bedrock), it was not possible to know if the addition of OM_{fossil} contributed to the increased Ad/Al values in GA soils. It was surprising that there was not a North to South gradient of soil $\Delta^{14}C$ values; they were all similar except for GA. Once again, GA soils were compositionally distinct from the rest of the samples.

Although the compositional information provided important insight into Fiordland soils, no logical basis for assigning sediments unique $\delta^{13}C_{terr}$ values was found after a close look at soil composition. In order to accomplish this, a larger number of soils would have to be sampled in order to determine if a North to South gradient in soil composition really exists or if GA soils are outliers due to the specific location they were sampled in. Therefore, it was concluded that assigning unique $\delta^{13}C_{terr}$ values to sediments, or selectively excluding/including $\delta^{13}C_{vegetation}$ values would introduce more bias into our terrestrial end-member determination than taking an average of all the samples analyzed. Because soils may in fact contain OM_{fossil} with a more enriched $\delta^{13}C$

value, an average was therefore taken of all vegetation types analyzed and used as a $\delta^{13}C_{terr}$ end-member value ($\delta^{13}C_{terr}$ = -30.21 ‰, n = 22).

OM_{fossil}

A major assumption of the biomarker regression method to determine $\delta^{13}C_{mar}$ is that a third source of OC is not present. Previous studies have shown that OM_{fossil} is delivered via rivers in significant quantities in the Southern Alps (Blair et al., 2010; Hilton et al., 2008). OM_{fossil} likely does not contain high yields of any recognizable biomarkers, and therefore its $\delta^{13}C$ signature ($\delta^{13}C_{fossil}$) may be influencing the $\delta^{13}C_{mar}$ value obtained from the x-axis intercept. To view the effect of OM_{fossil} on $\delta^{13}C_{mar}$, it was determined if any of this aged refractory carbon is present when the biomarker yields are zero.

While studies have shown that OM_{sed} consists of a spectrum of varying aged carbon (Torn et al., 2002; Trumbore, 1993; Eglinton et al, 1997; Pearson et al., 2001; Goñi et al., 2005), the main source of non-fossil OM in Fiordland is soils and vegetation with a modern $\Delta^{14}C$ signature. Therefore, deviations from sedimentary fm values of 1 (when corrected for ageing post-depositionally) were assumed to represent additions of OM_{fossil} from bedrock. This was further supported by low sedimentary [Ad/Al]v values. The percentage of OM_{fossil} present was therefore calculated as

$$\%OM_{fossil} = (1\text{-}fm)*100 \quad (8)$$

Using this equation, $\%OM_{fossil}$ contributions to sediments ranged from 2.5 (DC) to 15.9 % (CA) (x = 10.1 +/- 4.1, n = 12) (Appendix R). To determine the quantity of $\%OM_{fossil}$ present at zero biomarker concentrations, a linear least-squares regression was calculated

of lignin monomer yields vs. $\%OM_{fossil}$ (Fig. 20). The resulting strong negative correlation indicated a significant relationship between the amount of modern and fossil OMterr present, which is discussed further in a later section. The x-intercept of the graph suggested that 15.5% of theoretically biomarker free OM_{sed} is fossil in origin. This falls between the range of Southern Alp riverine POC percentages found by Hilton et al. (2008) (37%) and Blair et al. (2010) (0.25%), which is large and most likely related to bedrock type.

This quantity theoretically had a measurable effect on the biomarker-based $\delta^{13}C_{mar}$ estimates. However, complications again arose when choosing the $\delta^{13}C_{fossil}$ end-member. Hilton et al. (2008) measured a large range of $\delta^{13}C$ values in Southern Alp sedimentary bedrock (-18.85 to -26.17 ‰) north of Fiordland in approximately the middle of the western flank of the Southern Island. The mean value for n=10 bedrock samples was -21.1 +/- 1.1 ‰ (%OC = 0.15 +/- 0.05 %). In the Waiapoa River watershed, Blair et al. (2010) $\delta^{13}C_{fossil}$ values of -22.8 to -26.5 ‰ (x = -25.1 +/- 1.3 ‰, n=11), while in the same system Gomez et al. (2004) published an average value of -26.0 +- 1.2, n=11).

While $\delta^{13}C_{fossil}$ values from the Waiapoa River fell within the range of values obtained by Hilton et al. (2008) in the Southern Island, without additional analysis of sedimentary rocks from Fiordland the mean of $\delta^{13}C_{fossil}$ values from the western flank of the Southern Island was used to correct the biomarker-based $\delta^{13}C_{mar}$ values. While this value (-21.1 +/- 1.1 ‰, n=10) is not significantly different from the $\delta^{13}C_{mar}$ value of -20.71 +/- 2.09 ‰ (n=3) (p=0.67), it is still useful to correct the $\delta^{13}C_{mar}$ value, as this will

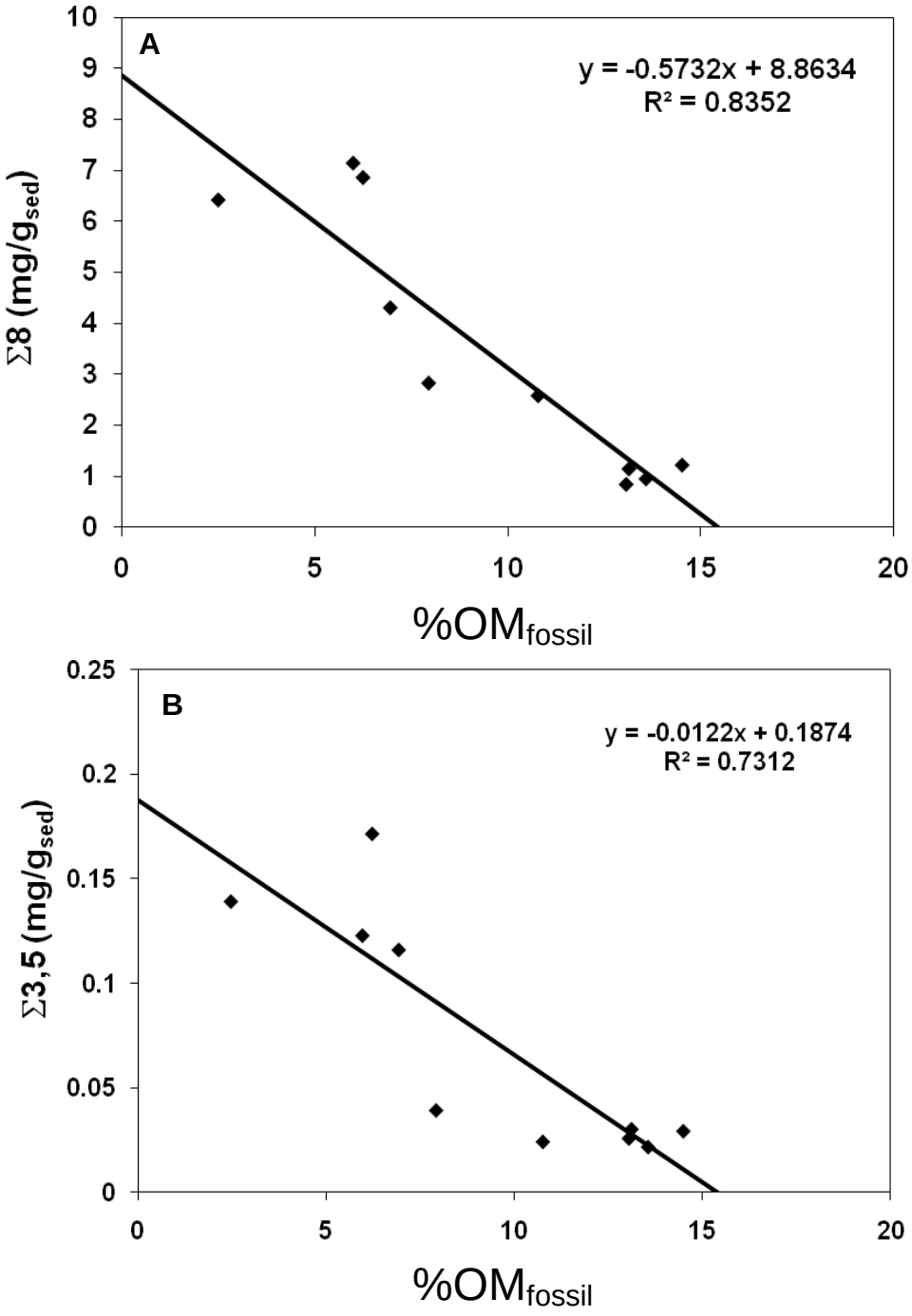

Figure 20. Linear least-squares regressions of dry sediment mass normalized lignin (Σ8; A) and 3,5-dihydroxybenzoic acid (Σ3,5; B) yields vs. Δ^{14}C-based $\%OM_{fossil}$ estimates.

ultimately effect the mean of end-member percentages during the final reconstruction. Assuming 15.5% OM_{fossil}, the new $\delta^{13}C_{mar}$ value rose to -20.63 ‰. This value was still not statistically different from $\delta^{13}C_{fossil}$, but was used as the final $\delta^{13}C_{mar}$ value.

Source Reconstruction : Marine, Terrestrial, Fossil

Due to the wide range of C/N values found in NZ OM_{fossil} (Blair et al., 2010; Gomez et al., 2004), and statistically similar $\delta^{13}C_{fossil}$ and $\delta^{13}C_{mar}$ values, a unique approach was used to separate out the relative abundances of marine, fossil, and modern OM_{terr}. First, a two end-member mixing model was constructed as follows:

$$\delta^{13}C_{meas} = \delta^{13}C_{mar} * f_{(mar+fossil)} + \delta^{13}C_{terr} * f_{terr} \quad (9)$$

where $\delta^{13}C_{meas}$ was the measured $\delta^{13}C$ value of bulk sedimentary organic carbon. Next, the two $\%OM_{fossil}$ values from each core were averaged to produce a static contribution for the core. This percentage was then subtracted from $f_{(mar+fossil)}*100$ to determine $\%OM_{mar}$.

This method was based on two assumptions; 1) $\delta^{13}C$ end-members of marine and fossil OC are statistically insignificant, and 2) fossil OC concentrations are constant downcore. The first assumption was proven valid in the previous section. The second assumption was not possible to prove within the limits of our dataset. However, % OM_{fossil} values among all cores (n=12) did not cover a wide range (2.49-15.89 %), and on average the % difference between the two samples measured in each core was 4.5%.

Overall, differences in % OM_{terr}, OM_{mar}, and OM_{fossil} were larger between sites (spatially) than temporally at each site (Fig. 21). The only discernable trend was an increase in the amount of OMmar over time at the CA site. Percentages of the marine,

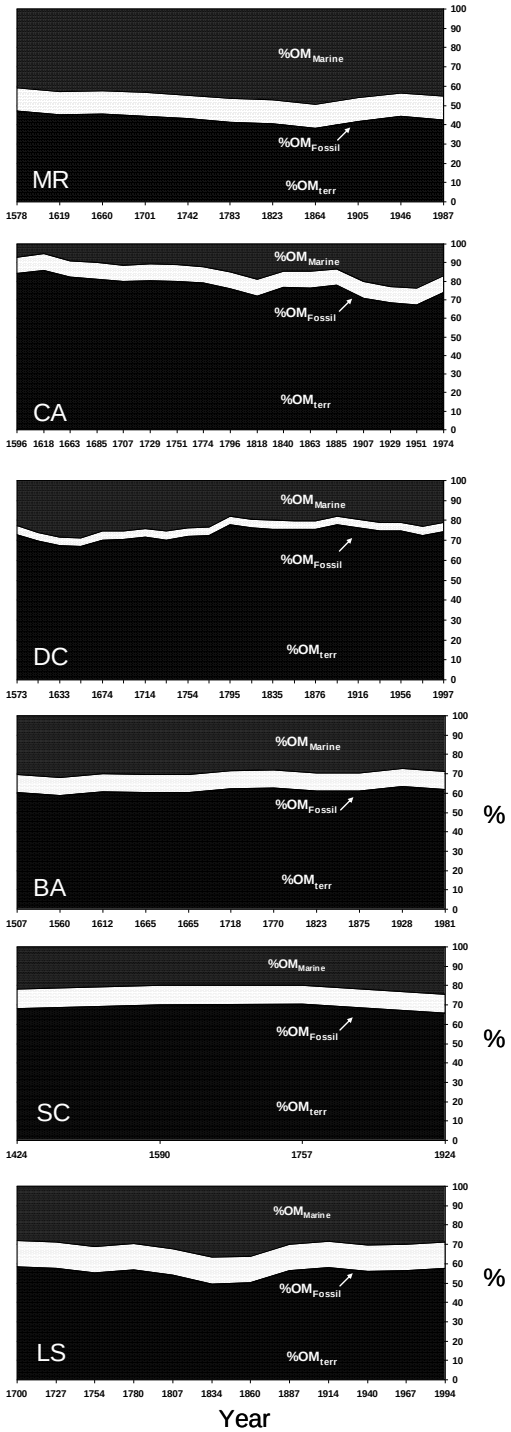

Figure 21. Historical source reconstruction. $\%OM_{terr}$ = the fraction of organic matter that is terrestrial in origin; $\%OM_{mar}$ = the fraction of organic matter that is marine in origin; $\%OM_{fossil}$ = the fraction of organic matter that is fossil in origin.

terrestrial, and fossil sources are listed in Appendix R. Terrestrial contributions ranged as high as 85.7% at CA to as low as 38.2% at MR. MR had the lowest relative terrestrial contributions overall (43.0 +/- 2.5, n=11) ranging from 38.2 to 47.0%. The site with the next lowest relative terrestrial contribution to sediments was LS (55.4 +/- 2.9%, n=12), with significantly higher values (>10%) than MR ($p < 0.05$). Values at this site ranged from 49.4 to 58.3%. BA (61.1 +/- 1.3, n=11) and SC (68.5 +/-2.2%) had a midrange of terrestrial contribution among all cores, which varied by only 5% at each of these sites. DC (73.1 +/- 3.2%) had a significantly higher relative terrestrial contribution, and a 10% difference between the highest and lowest values. CA contained the highest percentages of OM_{terr} (77.09 +/- 5.3), and also the largest range (67.3 to 85.7%).

The lack of any large trends or changes at each site with time, except for site CA which had larger marine contributions over time, may be due to the pristine watershed of Fiordland which has nearly 100% of its original forest intact (Leathwick et al., 2003). The large compositional differences in OM between cores is not observed in the biomarker source plots, suggesting that if the differences are due to variable delivery of OM_{terr} (as opposed to variations in OM_{mar} input), the quality of OM delivered does not change. If changes in the absolute amount of OM_{terr} delivered to these sites caused the observed spatial differences, it may be due to either 1) variations in fjord width, or 2) variations in landslide activity determined by topography. The first explanation is likely, as narrower regions at the fjord head concentrate delivered OM_{terr} into a smaller region, whereas more open sites effectively dilute OM_{terr}. This would explain why MR has the lowest relative OM_{terr} concentrations, as the core was taken from a very open location in

DS closer to the mouth of the fjord, while the other cores were taken from narrow basins close to the head of the fjords. To prove that variations in landslide activity was responsible for the observed trends, x-rays of the cores would be necessary, which would allow counts of the frequency and thickness of landslide layers at each site.

Another possible explanation for the observed differences between cores is variations in the absolute amount of OM_{mar} at each site. Increased contributions of OM_{mar} can be due to either increased preservation or increased delivery. Increased preservation of OM_{mar} would be more likely in basins near the head of the fjords that receive less input of new saltwater from the coast. This trend is not observed, with sites near the head having the lowest contributions of OM_{mar}. The more likely explanation is that production, and therefore delivery of OM_{mar}, is a function of fjord width as well, which determines the amount of incidence radiation available to phytoplankton. Schuller and Savage (unpublished data) used Variance Partitioning Analysis to show that the fjord light environment is the most important factor (22% of variance) controlling pigment concentrations, and therefore the absolute concentration of OM_{mar} in surface sediments. Therefore, fjord width may be controlling the relative amounts of OM_{mar} and OM_{terr} at sites from both ends, with narrow regions containing large amounts of OM_{terr} relative to OM_{mar}, and open regions with increased contributions of OM_{mar} and more diluted OM_{terr}. In fact, OM signatures have been shown to resemble more closely OM_{mar} in sediments towards the mouth of most fjords (Nuwer and Keil, 2005; Walsh et al., 2008; Smith et al., 2010).

Conclusion

12% of sediment deposited on continental margins in the last 100,000 years has been in temperate fjord systems (Syvitski et al., 1987). Nuwer and Keil (2005) found that due to a high concentration of OM_{terr} in the form of mineral-associated OM and organic debris (mostly woody material) in fjord sediments, they likely have contained more than 12% of organic material deposited over this time period. In this study it has been shown that Fiordland also contains large amounts of OM_{terr}, in the form of OM_{soil}, organic debris, and OM_{fossil}. Annual rainfall rates of several meters combined with steep topography and intact temperate rainforest sustained sediments that contained on average %OC composed of 64.9% terrestrial material and another % that was OM_{fossil} from sedimentary bedrock. Landslides are responsible for sediments that contain a large proportion of organic debris, and also contribute OM_{fossil} from mechanical erosion, which breaks down both organic debris and sedimentary bedrock into smaller size fractions.

Over the last ~500 years, OM_{terr} delivery to fjords has remained relatively unchanged. Spatial differences in the relative percentages of OM_{terr}, OM_{mar}, and OM_{fossil} were larger than differences downcore at each site. The unchanging proportions of OM at each location were due to the pristine watershed in Fiordland, which contains nearly 100% of its original forest. Spatial variations are thought to be caused primarily by the width of the fjord, as narrower regions near the head of the fjord have reduced plankton biomass due to topographic shading, and also concentrate OM_{terr} delivered by rain and landslides which is delivered to a smaller area.

This study supported the claim that fjords, with respect to other coastal environments, are disproportionately responsible for burying organic material, and should be considered when developing global carbon budgets.

CHAPTER V

CONCLUSIONS

The utility of the BIT Index is sensitive to the type of coastal environment with which it is being employed. In Fiordland, BIT Index values had a strong positive linear correlation with bulk carbon parameters, $\delta^{13}C$ and C/N, indicating the potential of the Index to quantify OMsoil in coastal sediments. However, modeled %OMsoil estimates as a function of branched tetraether concentrations revealed that mixing between marine and soil end-members is non-linear. Additionally, this method overestimates the amount of OMsoil present, with the degree of overestimation increasing with higher concentrations of branched GDGTs in soils and lower concentrations of crenarchaeol in sediments. It follows that the linear trend of the BIT Index and bulk carbon parameters in Fiordland is due to high crenarchaeol production in fjords and/or low production of branched-GDGT producing soil bacteria. The latter is the most likely case, as Fiordland soils are relatively shallow and immature due to frequent landslides. On the Louisiana Shelf, crenarchaeol concentrations in sediments controlled BIT Index values due to large seasonal changes in production and therefore ammonia. Fiordland, unlike many other fjord systems, is not glacier-fed and therefore does not have large seasonal changes in production, contributing to the linear trend seen in BIT Index values. However, due to the quantitative limitations of the index, it was not used in the historical reconstruction of terrestrial inputs to Fiordland.

Sedimentary OC concentrations in Fiordland were high compared to other types of coastal environments, similar to findings in other fjord systems. Spatial variations in bulk carbon and biomarker parameters were larger than temporal variations in the six cores taken. OMterr was the predominant fraction of OMsed in all but one site, followed by OMmar and then OMfossil from the weathering of sedimentary bedrock. High concentrations of OMterr in fjord sediments was due to an intact forested watershed, high annual rainfall rates, steep topography and frequent seismic activity, which resulted in both overland runoff containing POC from soils and landslides containing both POC from soils as well as from weathered sedimentary bedrock. The intact forested watershed also explained the minimal temporal variation on the OMterr concentration of sediments, as the watershed has experienced negligible deforestation and development. Spatial variations in the relative amounts of OMterr and OMmar are related to fjord width. Narrower, upstream regions of the fjord concentrate OMterr inputs over a smaller sedimentary area. Additionally, topographic shading inhibits production in these areas.

These results confirm the hypothesis that while fjords have contained 12% of sediments deposited to coastal zones over the last 100,000 years, they contain over 12% of the OM deposited to coastal zones over this time due to high concentrations of OMterr in sediments, both detrital and mineral-associated (Nuwer and Keil 2005).

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APPENDIX A

Bulk carbon parameters and BIT Index values of Doubtful Sound surface (0-2 cm) sediments.

Site	**DS01**	**DS03**	**DS04**	**DS06**	**DS07**	**DS08**	**DS09**	**DS10**
Latitude	-45.4625	-45.4607	-45.4573	-45.4672	-45.4134	-45.3832	-45.3698	-45.4074
Longitude	167.1637	167.1564	167.1525	167.0924	167.1122	167.0919	167.0196	166.9712
Depth(m)	18.9	N/A	75.4	93.3	141.7	278.7	184.6	64.3
% OC	10.1	3.2	7.7	11.4	4.3	7.4	10.1	9.1
$d^{13}C$	-28.7	-27.6	-27.9	-27.4	-26.9	-26.3	-27.8	-27.6
C/N	36.8	6.6	26.3	22.1	20.7	19.0	24.6	23.2
BIT	0.92	N/A	0.64	0.50	0.47	0.29	0.77	0.77
L8	5.76	9.65	6.01	6.03	8.15	5.95	4.70	6.31
(Ad/Al)v	0.23	0.23	0.20	0.21	0.97	0.20	0.20	0.20
(Ad/Al)s	0.20	0.18	0.16	0.16	0.99	0.18	0.17	0.16
C/V	0.10	0.09	0.08	0.12	0.66	0.05	0.06	0.06
S/V	1.24	1.32	1.30	1.30	1.00	1.32	1.23	1.26
mg 100mg OC^{-1}								
PAL	0.18	0.19	0.11	0.12	0.12	0.09	0.08	0.10
PON	0.10	0.06	0.04	0.05	0.04	0.03	0.02	0.03
VAL	1.63	2.58	1.61	1.63	2.25	1.62	1.31	1.75
ARS	2.21	2.19	2.16	2.61	2.08	2.16	2.33	2.24
EVAL	1.32	1.09	1.21	1.27	1.29	1.23	1.25	1.24
VON	0.47	0.77	0.47	0.46	0.62	0.43	0.37	0.48
PAD	0.12	0.10	0.06	0.06	0.07	0.05	0.04	0.05
SAL	2.09	3.44	2.21	2.23	2.93	2.10	1.63	2.32
VAD	0.37	0.60	0.32	0.34	0.51	0.34	0.27	0.36
SON	0.53	0.95	0.48	0.53	0.80	0.58	0.44	0.49
DAD	0.13	0.15	0.09	0.09	0.11	0.08	0.07	0.09
SAD	0.42	0.66	0.37	0.37	0.56	0.41	0.29	0.38
CAD	0.11	0.15	0.08	0.14	0.08	0.05	0.05	0.07
FAD	0.14	0.21	0.11	0.15	0.13	0.07	0.07	0.10

Site	**DS11**	**DS12**	**DS13**	**DS14**	**DS15**	**DS16**	**DS17**	**DS20**
Latitude	-45.3279	-45.3388	-45.3014	-45.2695	-45.2565	-45.2767	-45.2855	-45.3155
Longitude	167.013	166.9099	166.9842	166.9026	167.1626	167.1044	167.0181	167.1704
Depth(m)	96.4	N/A	75.4	135	37.6	41.5	182	42.8
% OC	2.0	9.3	0.6	1.8	4.6	1.6	1.9	4.4
$d^{13}C$	-25.3	-27.8	-24.3	-26	-27.2	-27.9	-25.5	-27.4
C/N	16.2	5.70	14.7	17.4	24.6	23.8	16.9	22.3
BIT	0.28	N/A	0.26	0.53	0.63	0.93	0.24	0.77
L8	2.73	7.73	3.91	4.45	7.25	11.20	5.09	6.73
(Ad/Al)v	0.25	0.23	0.25	0.21	0.19	0.24	0.26	0.24
(Ad/Al)s	0.20	0.18	0.20	0.17	0.16	0.20	0.21	0.19
C/V	0.05	0.07	0.05	0.05	0.05	0.10	0.05	0.07
S/V	1.09	1.12	1.03	1.33	1.18	1.02	1.20	1.23
mg 100mg OC^{-1}								
PAL	0.06	0.13	0.10	0.07	0.11	0.22	0.10	0.13
PON	0.02	0.05	0.02	0.01	0.04	0.07	0.02	0.04
VAL	0.80	2.30	1.17	1.27	2.18	3.39	1.44	1.91
ARS	1.91	3.46	2.55	2.40	2.41	3.00	2.41	2.60
EVAL	1.30	1.52	1.32	1.34	1.24	1.36	1.23	1.27
VON	0.21	0.67	0.33	0.34	0.60	1.03	0.42	0.53
PAD	0.03	0.07	0.06	0.04	0.05	0.12	0.06	0.08
SAL	0.88	2.58	1.23	1.74	2.61	3.55	1.70	2.35
VAD	0.20	0.52	0.29	0.27	0.41	0.80	0.37	0.45
SON	0.23	0.70	0.30	0.45	0.60	0.88	0.51	0.63
DAD	0.05	0.12	0.08	0.05	0.09	0.20	0.09	0.11
SAD	0.19	0.50	0.27	0.29	0.46	0.75	0.38	0.48
CAD	0.02	0.09	0.04	0.04	0.07	0.20	0.04	0.08
FAD	0.03	0.15	0.05	0.06	0.10	0.31	0.07	0.11

APPENDIX B

Bulk carbon parameters and BIT Index values of Fiordland core-top (0-2 cm) and terrestrial samples (soil and leaf-litter).

Site	**SC2**	**BA1**	**DC1**	**MR2**	**S1**	**S2**	**S3**	**S4**	**LL1**	**LL2**	**LL3**
Latitude	-45.7333	-45.5501	-45.4501	-45.3002	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Longitude	166.7168	166.9002	167.15	166.9666	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Depth (m)	301	168	94.0	407	N/A	N/A	N/A	N/A	N/A	N/A	N/A
% OC	3.1	4.2	6.2	2.7	13.4	12.0	14.4	6.7	39.8	36.8	45.4
$\delta^{13}C$	-26.8	-26.4	-27.6	-24.7	-30.7	-30.4	-30.2	-28.9	-29.9	-30.6	-31.4
C/N	24.0	19.4	21.9	15.4	N/A	N/A	N/A	N/A	N/A	N/A	N/A
BIT	N/A	N/A	N/A	N/A	1.00	1.00	1.00	1.00	N/A	N/A	N/A
L8	6.45	10.70	10.00	6.28	6.50	5.73	2.33	16.6	9.34	12.5	4.06
(Ad/Al)v	0.24	0.25	0.22	0.27	0.23	0.27	0.19	0.30	0.17	0.16	0.16
(Ad/Al)s	0.17	0.19	0.17	0.22	0.21	0.24	0.17	0.22	0.14	0.15	0.16
C/V	0.08	0.06	0.09	0.06	0.16	0.20	0.05	0.07	0.15	0.11	0.08
S/V	1.29	1.34	1.32	1.28	0.50	0.41	1.14	0.98	1.23	0.90	1.08
mg 100mg OC^{-1}											
PAL	0.12	0.15	0.20	0.12	0.19	0.16	0.54	0.30	0.20	0.77	0.13
PON	0.04	0.05	0.07	0.03	0.05	0.05	0.16	0.07	0.04	0.50	0.05
VAL	1.73	2.85	2.71	1.69	2.67	2.30	8.07	4.96	2.82	4.40	1.29
ARS	3.05	3.52	3.72	2.00	2.65	2.60	3.39	4.42	3.31	6.69	3.76
EVAL	1.25	1.32	1.56	1.06	1.39	1.09	1.56	1.36	1.26	1.61	1.47
VON	0.56	0.84	0.84	0.50	0.74	0.70	1.92	1.32	0.62	1.12	0.39
PAD	0.07	0.10	0.11	0.08	0.10	0.10	0.35	0.15	0.12	0.33	0.11
SAL	2.36	3.90	3.68	2.18	1.41	1.04	5.48	5.26	3.51	4.04	1.52
VAD	0.40	0.69	0.58	0.45	0.62	0.64	1.71	1.47	0.47	0.72	0.21
SON	0.57	1.02	0.93	0.62	0.31	0.22	1.32	1.17	0.81	0.97	0.28
DAD	0.14	0.17	0.18	0.10	0.32	0.28	0.76	0.18	0.13	0.47	0.20
SAD	0.44	0.80	0.68	0.50	0.30	0.26	1.14	1.15	0.49	0.62	0.24
CAD	0.09	0.10	0.15	0.06	0.10	0.12	0.28	0.14	0.40	0.38	0.09
FAD	0.12	0.15	0.22	0.09	0.55	0.62	0.63	0.42	0.17	0.32	0.06

APPENDIX C

Bulk carbon, BIT Index values, and lignin parameters between surface samples taken at deep (> 90 m) and shallow (< 90 m) sites. * Indicates parameters with significant differences between shallow and deep sites.

		Depth*	BIT*	$\Lambda 8$	$(Ad/Al)_v$	% OC	C/N	$\delta^{13}C$
Shallow	**Avg**	50.8	0.70	7.73	6.74	5.5	24.5	-27.3
	Std. Dev.	21.3	0.23	2.23	2.24	3.6	6.6	1.4
Deep	**Avg**	159	0.44	6.10	5.30	5.5	19.6	-26.5
	Std. Dev.	59.3	0.19	2.16	2.68	4.1	3.1	0.9
t-test	***p***	0.0007	0.036	0.189	0.2	0.97	0.096	0.218

APPENDIX D

Biomarker results from cores $8C_{apr}$, $BC1_{apr}$, $BC1_{july}$ and $8C_{july}$ on the Louisiana Continental Shelf.

Core	Depth (cm)	BIT Index	$GDGT_{cren}$	$GDGT_{soil}$	$\Sigma 8_{10}$	LPVI	[Ad/Al]v	3,5:g
$8C_{apr}$	0-2	0.10	587	62.0	0.03	48.4	0.29	b.d
	2-4	0.10	567	65.1	0.35	71.2	0.23	0.54
	4-6	0.10	462	53.4	0.28	79.5	0.22	0.49
	6-8	0.26	282	99.7	0.30	75.2	0.19	b.d.
	8-10	0.40	219	145	0.83	91.3	0.17	0.91
	10-12	0.41	78.5	54.2	0.13	62.7	0.32	0.44
	12-14	0.36	144	80.2	0.09	75.0	0.26	0.27
$BC1_{apr}$	0-2	0.10	1360	148	0.37	122	0.22	1.00
	2-4	0.45	298	248	0.73	125	0.21	1.39
	4-6	0.10	997	116	0.87	107	0.18	1.16
	6-8	0.10	669	76.3	0.71	113	0.21	0.42
	8-10	0.12	615	87.8	0.36	122	0.22	0.58
	10-12	0.13	524	81.7	0.33	101	0.21	0.56
	12-14	0.09	440	44.9	0.27	51.3	0.20	0.54
	14-16	0.11	185	22.4	0.24	93.1	0.25	0.61
	16-18	0.26	331	117	0.22	102	0.24	0.30
	18-20	0.20	480	114	n.n	n.m	n.m	n.m
$BC1_{july}$	0-2	0.08	1390	128	0.24	113	0.26	0.80
	2-4	0.11	1080	129	0.07	51.5	0.20	b.d.
	4-6	0.10	567	64.4	0.23	89.0	0.24	0.40
	6-8	0.10	593	64.3	0.12	125	0.29	0.40
	8-10	0.12	471	65.1	0.09	89.4	0.25	0.24
	10-12	0.08	669	56.3	0.06	70.2	0.28	0.14
	12-14	0.09	897	89.8	0.36	131	0.26	0.96
	14-16	0.15	827	140	0.29	88.6	0.27	0.59
	16-18	0.12	954	132	0.32	116	0.27	0.73
	18-20	0.13	599	85.8	0.29	93.0	0.33	0.65
$8C_{july}$	0-2	0.10	850	99.4	0.40	55.2	0.22	0.45
	2-4	0.11	699	84.9	0.20	80.2	0.22	0.28
	4-6	0.12	411	58.0	0.39	77.5	0.18	0.37
	6-8	0.15	418	71.2	0.19	81.9	0.18	0.26
	8-10	0.14	275	44.3	0.13	76.6	0.26	0.21
	10-12	0.46	104	86.9	0.01	66.4	0.76	b.d.
	12-14	0.34	137	69.6	0.10	57.2	0.34	0.28
	14-16	0.42	89.5	63.8	0.16	61.2	0.24	0.44
	16-18	0.48	73.7	68.0	0.25	70.0	0.24	0.45
	18-20	0.35	117	64.3	0.17	86.5	0.24	b.d.

APPENDIX E

Linear regression statistics between GDGT-based proxies and CuO based proxies. The larger R^2 value for each core is in bold.

Core	R^2 BIT vs. $\Sigma 8_{10}$	R^2 $GDGT_{soil}$ vs. $\Sigma 8_{10}$
All	0.00	**0.27**
$8C_{apr}$	0.08	**0.68**
$BC1_{apr}$	0.06	**0.24**
$BC1_{july}$	0.09	**0.17**
$8C_{july}$	**0.29**	0.03

Core	R^2 BIT vs. 3,5:g	R^2 $GDGT_{soil}$ vs. 3,5:g
All	0.00	**0.34**
$8C_{apr}$	0.11	**0.18**
$BC1_{apr}$	0.20	**0.54**
$BC1_{july}$	0.01	**0.18**
$8C_{july}$	**0.04**	0.00

APPENDIX F

Linear regression statistics of the BIT Index vs. $GDGT_{cren}$ and $GDGT_{soil}$ are shown in order to determine what value is controlling the BIT Index. The regression producing the highest R^2 value in each core is in bold.

Core	R^2 BIT vs. $GDGT_{cren}$	R^2 BIT vs. $GDGT_{soil}$
All	**0.72**	0.03
$8C_{apr}$	**0.82**	0.28
$BC1_{apr}$	0.21	**0.38**
$BC1_{july}$	0.05	**0.15**
$8C_{july}$	**0.94**	0.01

APPENDIX G

GDGT data from Belicka and Harvey (2009). $\%OM_{soil}$ (BIT) represents the estimates that were made from that study by multiplying the BIT Index by 100 (equation (4), this text. To minimize the influence of crenarchaeol concentrations and to avoid non-linear mixing, equation (6) from this study is applied to the GDGT data set to produce a corrected estimate of $\%OM_{soil}$ (brGDGTs). $\Delta\%$ indicates the direction and magnitude of change by using the new equation, which in generally causes a decrease in $\%OM_{soil}$ estimates.

Station	GDGT-I	GDGT-II	GDGT-III	GDGT-IV	BIT Index	$GDGT_{soil}$	$\%OM_{soil}$ (BIT)	$\%OM_{soil}$ (brGDGTs)	$\Delta\%$
STN-1	0.6	1.2	1	17.9	0.13	2.8	13	4.9	-8.1
WHS-2	0.7	1.2	1.8	73.4	0.05	3.7	5	6.4	1.4
WHS-5	0.1	0.1	0.2	10.5	0.03	0.4	3	0.7	-2.3
WHS-6	0.1	tr	0.1	2.1	0.07	0.2	7	0.3	-6.7
WHS-7	0.4	0.5	0.7	16.7	0.09	1.6	9	2.8	-6.2
WHS-12	0.3	0.1	0.1	0.6	0.46	0.5	46	0.9	-45.1
EHS-4	0.1	0.1	0.2	7.2	0.05	0.4	5	0.7	-4.3
EHS-6	0.3	0.3	0.5	36.9	0.03	1.1	3	1.9	-1.1
EHS-9	0.4	0.5	0.7	40.4	0.04	1.6	4	2.8	-1.2
EHS-11	0.9	1.1	1.4	64.1	0.05	3.4	5	5.9	0.9
EHS-12	0.1	0.1	0.9	6.9	0.13	1.1	13	1.9	-11.1
BC-3	0.9	2	1.9	22.3	0.18	4.8	18	8.3	-9.7
BC-4	1.3	2.4	2.1	47.6	0.11	5.8	11	10.1	-0.9
BC-5	0.7	1	0.8	17.3	0.12	2.5	12	4.3	-7.7
BC-7	0.2	0.4	0.4	24.3	0.04	1.0	4	1.7	-2.3
EB-2	0.4	0.7	0.6	7.4	0.19	1.7	19	2.9	-16.1
EB-4	0.7	1.6	1.4	9.6	0.28	3.7	28	6.4	-21.6
EB-7	0.3	0.1	0.1	3.8	0.11	0.5	11	0.9	-10.1
Ik Riv.	5.6	23.1	29	nf	1.00	58	100	100	0

APPENDIX H

Bulk elemental and isotopic data for vegetation and soil samples collected in Fiordland, NZ. U.I = unidentified, N/A = not applicable, - = not measured.

Type	Label	ID	%OC	δ13C	N/C	C/N	$\Delta^{14}C$	f_m
Submerged Wood	SUW-1	U.I.	40.9	-26.64	0.0087	114	-	-
	SUW-2	U.I.	42.1	-26.89	0.0028	352	-	-
	SUW-3	U.I.	30.8	-26.88	0.0128	78.2	-	-
Angiosperm Wood	AW-MH	Mountain Horopito	48.6	-30.27	0.0086	116	-	-
	AW-SB	Silver Beech	45.5	-31.50	0.0092	108	-	-
Gynmosperm Wood	GW-T	Totara	49.6	-29.69	0.0012	825	-	-
Angiosperm Bark	AB-SB	Silver Beech	60.1	-34.91	0.0114	87.7	-	-
Gynmosperm Bark	GB-T	Totara	51.6	-32.20	0.0051	197	-	-
Angiosperm Leaves	AL-MH	Mountain Horopito	50.1	-31.95	0.0193	51.7	-	-
	$AL\text{-}SB_G$	Silver Beech	51.1	-33.23	0.0215	46.6	-	-
	$AL\text{-}SB_B$	Silver Beech	52.2	-31.26	0.0220	45.5	-	-
	$AL\text{-}FF_{AG}$	Five-Fingers	44.7	-33.51	0.0471	21.2	-	-
	$AL\text{-}FF_{FY}$	Five-Fingers	41.7	-32.11	0.0222	45.1	-	-
	$AL\text{-}FF_{FB}$	Five-Fingers	49.3	-34.38	0.0107	93.3	-	-
Gymnosperm Needles	GN-T	Totara	49.9	-33.80	0.0090	112	-	-
Leaf Litter	LL	U.I.	44.1	-30.20	0.0216	46.4	-	-
Fern Non-woody	F-NW	U.I.	47.9	-31.18	0.0447	22.4	-	-
Fern Woody	F-W	U.I.	46.7	-29.95	0.0217	46.2	-	-
Moss	M	U.I.	31.8	-29.81	0.0307	32.6	-	-
Grass	G	U.I.	45.2	-27.61	0.0199	50.3	-	-
Epiphytes	E-1	U.I.	38.3	-31.16	0.0209	47.8	-	-
	E-2	U.I.	46.6	-30.24	0.0079	126	-	-
Soils	S-GA1	N/A	3.07	-26.48	0.0733	13.6	-	-
	S-GA2	N/A	2.06	-26.89	0.0848	11.8	70.22	1.08
	S-DC1	N/A	3.04	-28.64	0.0659	15.2	-	-
	S-DC2	N/A	14.5	-28.76	0.0706	14.2	127.7	1.14
	S-DC3	N/A	0.84	-27.07	0.0647	15.4	-	-
	S-DS	N/A	42.1	-30.18	0.0437	22.9	128.5	1.14
	S-PI1	N/A	49.1	-29.53	0.0226	44.3	128.5	1.14
	S-PI2	N/A	48.2	-29.33	0.0270	37.0	-	-

APPENDIX I

Bulk elemental and isotopic data for sediment samples collected in Fiordland, NZ. U.I = unidentified, N/A = not applicable, - = not measured.

Core	Lat (S)	Long (E)	Depth (m)	LSR (cm y^{-1})	Depth (cm)	Year	%OC	δ13C	N/C	C/N	$\Delta^{14}C$	f_m	f_m(CT)
MR2	45º18.6251'	166º58.0379'	407	0.049	0-2	1987	4.13	-24.70	0.0708	14.1	-	-	-
					2-4	1946	4.00	-24.86	0.0696	14.4	-	-	-
					4-6	1905	3.90	-24.63	0.0666	15.0	-	-	-
					6-8	1864	3.60	-24.29	0.0715	14.0	-129.9	0.88	0.89
					8-10	1823	3.69	-24.52	0.0708	14.1	-	-	-
					10-12	1783	3.72	-24.59	0.0696	14.4	-	-	-
					12-14	1742	3.66	-24.76	0.0686	14.6	-	-	-
					14-16	1701	3.54	-24.88	0.0672	14.9	-	-	-
					16-18	1660	3.45	-24.98	0.0664	15.1	-176.12	0.83	0.86
					18-20	1619	3.54	-24.94	0.0667	15.0	-	-	-
					20-22	1578	3.56	-25.13	0.0638	15.7	-	-	-
CA4	45º24.1444'	166º58.9259'	85	0.090	2-4	1974	7.83	-27.73	0.0491	20.4	-	-	-
					4-6	1951	10.8	-27.08	0.0436	22.9	-71.68	0.94	0.94
					6-8	1929	9.92	-27.17	0.0436	22.9	-	-	-
					8-10	1907	6.88	-27.41	0.0395	25.3	-	-	-
					10-12	1885	8.26	-28.08	0.0353	28.3	-176.38	0.83	0.84
					12-14	1863	7.48	-27.93	0.0333	30.1	-	-	-
					14-16	1840	6.74	-27.96	0.0356	28.1	-	-	-
					16-18	1818	6.73	-27.52	0.0408	24.5	-	-	-
					18-20	1796	4.91	-27.91	0.0402	24.9	-	-	-
					20-22	1774	6.60	-28.19	0.0260	38.5	-	-	-
					22-24	1751	4.50	-28.28	0.0389	25.7	-	-	-
					24-26	1729	4.31	-28.32	0.0506	19.8	-	-	-
					26-28	1707	4.54	-28.26	0.0507	19.7	-	-	-
					28-30	1685	3.93	-28.41	0.0480	20.8	-	-	-
					30-32	1663	2.62	-28.49	0.0480	20.9	-	-	-
					34-36	1618	8.61	-28.84	0.0227	44.0	-	-	-
					36-38	1596	8.50	-28.68	0.0245	40.7	-	-	-
DC1	45º27.4767'	167º09.2441'	94	0.099	0-2	1997	8.73	-27.76	0.0419	23.8	-	-	-
					2-4	1977	8.60	-27.58	0.0387	25.9	-34.26	0.97	0.98
					4-6	1956	6.11	-27.78	0.0424	23.6	-	-	-
					6-8	1936	7.02	-27.79	0.0399	25.1	-	-	-
					8-10	1916	8.11	-27.94	0.0313	32.0	-	-	-
					10-12	1896	7.38	-28.09	0.0306	32.7	-80.64	0.93	0.94
					12-14	1876	10.0	-27.87	0.0343	29.2	-	-	-
					14-16	1855	11.3	-27.85	0.0356	28.1	-	-	-
					16-18	1835	10.7	-27.87	0.0370	27.0	-	-	-
					18-20	1815	11.4	-27.92	0.0345	28.9	-	-	-
					20-22	1795	8.37	-28.08	0.0317	31.5	-	-	-
					22-24	1775	7.57	-27.56	0.0462	21.6	-	-	-
					24-26	1754	8.42	-27.51	0.0450	22.2	-	-	-
					26-28	1734	8.48	-27.35	0.0506	19.8	-	-	-
					28-30	1714	9.83	-27.49	0.0480	20.8	-	-	-
					30-32	1694	9.30	-27.37	0.0513	19.5	-	-	-
					32-34	1674	9.48	-27.35	0.0489	20.5	-	-	-
					34-36	1653	9.41	-27.05	0.0518	19.3	-	-	-
					36-38	1633	9.07	-27.07	0.0485	20.6	-	-	-
					40-42	1593	8.38	-27.29	0.0553	18.1	-	-	-
					42-44	1573	7.05	-27.61	0.0541	18.5	-	-	-
BA1	45º33.5850'	166º54.7416'	168	0.038	0-2	1981	6.08	-26.54	0.0529	18.9	-	-	-
					2-4	1928	4.51	-26.70	0.0514	19.5	-119.93	0.89	0.89
					4-6	1875	4.59	-26.48	0.0519	19.3	-97.87	0.91	0.92
					6-8	1823	5.23	-26.49	0.0515	19.4	-	-	-
					8-10	1770	6.03	-26.64	0.0485	20.6	-	-	-
					10-12	1718	6.20	-26.59	0.0494	20.2	-	-	-
					12-14	1665	5.78	-26.40	0.0516	19.4	-	-	-
					14-16	1612	6.07	-26.45	0.0507	19.7	-	-	-
					16-18	1560	6.10	-26.27	0.0519	19.3	-	-	-
					18-20	1507	5.54	-26.40	0.0503	19.9	-	-	-
SC2	45º44.0007'	166º43.6567'	301	0.012	0-2	1924	3.53	-26.91	0.0495	20.2	-	-	-
					2-4	1757	1.94	-27.36	0.0462	21.6	-154.53	0.85	0.87
					4-6	1590	6.29	-27.34	0.0428	23.4	-	-	-
					6-8	1424	6.36	-27.16	0.0445	22.5	-131.85	0.87	0.93
LS1	45º59.0507'	166º48.6033'	370	0.075	0-2	1994	4.75	-26.14	0.0542	18.5	-	-	-
					2-4	1967	4.68	-26.02	0.0526	19.0	-	-	-
					4-6	1940	4.11	-25.99	0.0515	19.4	-	-	-
					6-8	1914	3.42	-26.18	0.0487	20.5	-159.6	0.85	0.85
					8-10	1887	3.56	-26.02	0.0529	18.9	-	-	-
					10-12	1860	4.10	-25.43	0.0547	18.3	-	-	-
					12-14	1834	3.77	-25.36	0.0576	17.4	-154.58	0.85	0.87
					14-16	1807	3.56	-25.80	0.0517	19.3	-	-	-
					16-18	1780	4.20	-26.07	0.0518	19.3	-	-	-
					18-20	1754	5.11	-25.91	0.0518	19.3	-	-	-
					20-22	1727	3.65	-26.13	0.0554	18.0	-	-	-
					22-24	1700	3.09	-26.21	0.0530	18.9	-	-	-

APPENDIX J

Lignin-phenol proxies and yields normalized to g dry sediment (Σ) and 100 mg OC (Λ) of Fiordland, NZ vegetation and soils.

Sample	Σ8	ΣL	Σ3,5-Bd	Λ_8	ΛL	Λ3,5-Bd	[Ad/Al]v	[Ad/Al]s	P/(V+S))	C/V	S/V	LPVI
SUW-1	14.9	61.1	127	31.0	0.11	0.36	0.00	0.01	1.29	73.9	0.00	0.06
SUW-2	23.4	98.5	181	42.9	0.15	0.16	0.00	0.01	2.07	139	0.01	0.24
SUW-3	25.0	77.0	163	53.1	0.19	0.18	0.00	0.03	1.17	66.5	0.00	0.06
AW-MH	9.31	45.2	75.2	15.5	0.13	0.14	0.02	0.08	2.92	258	0.05	0.55
AW-SB	17.2	78.3	115	25.3	0.11	0.26	0.00	0.01	5.21	420	0.00	0.05
GW-T	11.0	54.4	180	36.4	0.15	0.36	0.03	0.01	0.01	1.03	0.00	0.09
AB-SB	2.25	13.5	30.8	5.13	0.20	0.19	0.03	0.30	0.57	110	0.08	0.56
GB-T	5.96	30.7	91.6	17.8	0.18	0.19	0.09	0.06	0.12	3.25	0.03	0.81
AL-MH	1.58	7.89	15.1	3.02	0.17	0.19	0.05	0.46	1.22	521	0.05	0.16
$AL\text{-}SB_G$	8.55	43.8	85.3	16.7	0.15	0.16	0.02	0.08	1.56	122	0.02	0.39
$AL\text{-}SB_B$	9.28	48.4	95.8	18.3	0.15	0.18	0.02	0.03	1.53	98.4	0.02	0.44
$AL\text{-}FF_{AG}$	1.22	5.46	13.3	2.97	0.16	0.17	0.14	0.14	0.53	40.8	0.02	0.06
$AL\text{-}FF_{FY}$	3.54	14.8	32.0	7.67	0.16	0.16	0.09	0.37	0.70	194	0.00	0.03
$AL\text{-}FF_{FB}$	3.70	18.3	37.4	7.59	0.16	0.19	0.03	0.12	1.23	113	0.15	1.19
GN-T	3.42	17.1	48.7	9.76	0.28	0.37	0.32	0.06	0.21	6.40	0.12	1.67
LL	8.10	35.7	75.1	17.0	0.16	0.16	0.03	0.06	1.18	76.5	0.04	0.60
F-NW	2.40	11.5	35.2	7.35	0.17	0.00	0.75	0.13	0.00	2.53	0.02	0.21
F-W	8.05	37.6	124.1	26.6	0.15	0.00	0.05	0.01	0.00	1.03	0.00	0.16
M	1.31	4.16	8.84	2.78	0.20	0.31	0.32	0.79	0.31	181	0.16	0.32
G	3.05	13.8	22.8	5.04	0.12	0.28	0.03	1.36	1.47	2766	0.00	0.01
E-1	0.09	0.34	0.76	0.20	0.70	0.00	2.87	0.76	0.12	67.5	5.68	1.02
E-2	0.03	0.14	0.32	0.07	0.20	0.00	1.80	0.74	0.14	66.9	1.54	0.12
S-GA1	1.19	0.37	0.88	2.85	0.67	0.65	0.18	0.32	0.37	68.0	0.17	0.04
S-GA2	1.78	0.37	0.78	3.77	0.67	0.69	0.12	0.22	0.98	148	0.16	0.03
S-DC1	1.06	0.45	1.09	2.60	0.56	0.39	0.17	0.21	0.44	48.4	0.13	0.04
S-DC2	5.00	7.54	18.8	12.5	0.31	0.26	0.07	0.09	0.51	27.5	0.04	0.17
S-DC3	2.35	0.19	0.44	5.52	0.30	0.25	0.12	0.12	0.67	50.4	0.12	0.01
S-DS	3.00	10.8	25.9	7.22	0.47	0.36	0.09	0.15	0.55	46.0	0.07	0.43
S-PI1	4.28	22.0	51.0	9.91	0.26	0.26	0.04	0.11	0.73	51.2	0.10	1.23
S-PI2	5.80	20.6	49.4	13.9	0.29	0.28	0.07	0.10	0.62	39.8	0.12	1.47

APPENDIX K

Lignin-phenol proxies and yields normalized to g dry sediment (Σ) and 100 mg OC (Λ) of Fiordland, NZ sediments.

Core	Depth (cm)	Σ8	ΣL	Σ3,5-Bd	Λ_8	ΛL	Λ3,5-Bd	[Ad/Al]v	[Ad/Al]s	P/(V+S))	C/V	S/V	LPVI
MR2	0-2	4.22	8.71	0.08	10.2	21.1	0.04	0.29	0.24	0.04	0.05	1.28	82.8
	2-4	1.46	2.92	0.03	3.65	7.29	0.06	0.31	0.21	0.04	0.07	1.42	104
	4-6	2.23	4.68	0.05	5.73	12.0	0.05	0.28	0.21	0.04	0.06	1.19	78.3
	8-10	1.22	2.43	0.03	3.31	6.59	0.06	0.32	0.21	0.04	0.07	1.44	105
	10-12	1.23	2.44	0.03	3.31	6.55	0.06	0.30	0.20	0.04	0.07	1.48	107
	12-14	2.37	4.87	0.06	6.48	13.3	0.06	0.32	0.28	0.04	0.06	1.3	86.5
	14-16	1.23	2.39	0.03	3.47	6.76	0.07	0.31	0.22	0.04	0.11	1.53	135
	16-18	0.96	1.88	0.02	2.78	5.46	0.06	0.36	0.21	0.04	0.09	1.52	121
	18-20	1.54	3.11	0.04	4.34	8.79	0.06	0.31	0.24	0.04	0.07	1.35	96.9
	20-22	1.50	3.13	0.03	4.22	8.78	0.05	0.27	0.22	0.04	0.05	1.24	77.3
CA4	2-4	5.71	11.2	0.20	7.29	14.3	0.10	0.25	0.23	0.03	0.12	1.47	148
	4-6	7.15	14.3	0.12	6.65	13.3	0.04	0.26	0.22	0.03	0.09	1.41	110
	6-8	6.88	13.8	0.11	6.93	13.9	0.04	0.28	0.25	0.04	0.08	1.4	107
	8-10	5.51	10.6	0.10	8.02	15.4	0.05	0.24	0.18	0.05	0.07	1.65	127
	22-24	3.45	6.72	0.05	7.66	14.9	0.04	0.22	0.16	0.02	0.06	1.59	114
	24-26	2.73	5.42	0.07	6.35	12.6	0.06	0.24	0.18	0.03	0.09	1.46	115
	26-28	2.42	5.01	0.06	5.33	11.0	0.06	0.25	0.19	0.04	0.09	1.21	94.7
	30-32	2.34	4.79	0.04	8.92	18.3	0.04	0.21	0.17	0.03	0.09	1.28	98.4
	34-36	9.03	16.9	0.10	10.5	19.6	0.03	0.18	0.15	0.01	0.04	1.88	134
	36-38	7.17	13.6	0.07	8.44	16.1	0.03	0.19	0.15	0.01	0.04	1.76	121
DC1	0-2	7.08	14.8	0.20	8.11	16.9	0.06	0.73	0.38	0.04	0.12	1.14	103
	2-4	6.43	13.1	0.14	7.47	15.3	0.05	0.28	0.24	0.04	0.1	1.27	102
	4-6	3.78	7.46	0.08	6.19	12.2	0.05	0.36	0.24	0.05	0.15	1.41	153
	6-8	4.55	9.28	0.09	6.48	13.2	0.05	0.24	0.20	0.04	0.09	1.3	99.3
	8-10	5.14	10.5	0.11	6.33	12.9	0.05	0.24	0.20	0.04	0.12	1.25	114
	10-12	6.87	14.5	0.17	9.30	19.6	0.06	0.23	0.22	0.05	0.09	1.12	82.6
	12-14	5.85	12.1	0.18	5.83	12.1	0.07	0.31	0.25	0.05	0.11	1.19	104
	14-16	5.35	10.6	0.17	4.73	9.40	0.08	0.33	0.26	0.05	0.21	1.29	202
	16-18	6.14	12.5	0.20	5.74	11.7	0.08	0.41	0.30	0.04	0.11	1.28	110
	18-20	5.77	11.8	0.18	5.07	10.4	0.07	0.50	0.30	0.04	0.09	1.27	98.1
	20-22	5.79	11.9	0.12	6.92	14.3	0.05	0.24	0.22	0.03	0.08	1.25	90.4
	22-24	3.73	7.70	0.08	4.93	10.2	0.05	0.21	0.18	0.04	0.07	1.25	88.1
	24-26	5.62	11.5	0.13	6.68	13.7	0.05	0.27	0.23	0.04	0.08	1.29	97
	26-28	6.26	12.5	0.11	7.39	14.8	0.04	0.23	0.19	0.04	0.08	1.42	106
	28-30	5.61	11.2	0.11	5.70	11.4	0.05	0.23	0.18	0.04	0.08	1.42	108
	30-32	5.99	12.1	0.15	6.44	13.0	0.1	0.32	0.26	0.04	0.1	1.32	111
	32-34	5.44	11.1	0.12	5.74	11.7	0.05	0.24	0.19	0.05	0.09	1.3	103
	34-36	7.65	15.5	0.17	8.14	16.5	0.06	0.24	0.20	0.05	0.09	1.34	105
	36-38	5.04	10.1	0.11	5.56	11.2	0.06	0.24	0.19	0.04	0.09	1.36	108
	40-42	4.74	9.53	0.10	5.66	11.4	0.05	0.23	0.19	0.04	0.09	1.37	109
	42-44	5.74	11.9	0.18	8.14	16.8	0.07	0.27	0.21	0.05	0.11	1.21	102
BA1	0-2	5.31	10.8	0.10	8.73	17.8	0.04	0.29	0.25	0.03	0.06	1.33	89.2
	2-4	2.59	5.31	0.02	5.74	11.8	0.02	0.30	0.27	0.03	0.05	1.32	84.4
	4-6	2.84	5.75	0.04	6.18	12.5	0.03	0.42	0.26	0.03	0.06	1.36	93.4
	6-8	3.81	7.73	0.06	7.28	14.8	0.04	0.25	0.22	0.03	0.05	1.36	89.2
	8-10	4.25	8.66	0.09	7.55	15.4	0.05	0.37	0.25	0.03	0.06	1.33	90.6
	10-12	4.61	9.38	0.08	7.43	15.1	0.04	0.27	0.23	0.03	0.05	1.35	87.9
	12-14	3.92	8.09	0.08	6.79	14.0	0.05	0.28	0.23	0.03	0.05	1.28	82.7
	14-16	3.94	8.14	0.07	6.49	13.4	0.04	0.29	0.20	0.03	0.05	1.27	80.6
	16-18	3.56	7.33	0.07	5.84	12.0	0.04	0.25	0.21	0.03	0.05	1.29	83
	18-20	3.15	6.51	0.06	5.71	11.8	0.05	0.25	0.22	0.03	0.05	1.27	81.1
SC2	0-2	1.93	3.91	0.05	5.48	11.1	0.07	0.43	0.30	0.05	0.1	1.34	111
	2-4	0.85	1.70	0.03	4.39	8.74	0.08	0.33	0.22	0.04	0.11	1.4	127
	4-6	2.76	5.49	0.07	4.39	8.73	0.07	0.41	0.27	0.05	0.15	1.36	152
	6-8	4.31	8.53	0.12	6.78	13.4	0.07	0.38	0.25	0.04	0.14	1.41	147
LS1	0-2	1.08	2.09	0.03	2.27	4.40	0.07	0.43	0.25	0.04	0.11	1.56	144
	2-4	1.50	2.93	0.04	3.21	6.25	0.07	0.31	0.20	0.04	0.08	1.56	120
	4-6	1.34	2.61	0.03	3.25	6.34	0.07	0.31	0.21	0.04	0.08	1.55	122
	6-8	1.23	2.39	0.03	3.60	6.98	0.06	0.29	0.19	0.03	0.08	1.59	125
	8-10	1.60	3.21	0.04	4.50	9.03	0.06	0.27	0.22	0.03	0.05	1.43	95.7
	10-12	1.09	2.10	0.03	2.65	5.12	0.07	0.44	0.26	0.04	0.1	1.58	136
	12-14	1.16	2.25	0.03	3.07	5.97	0.07	0.32	0.20	0.04	0.08	1.58	121
	14-16	1.15	2.23	0.03	3.24	6.26	0.07	0.31	0.20	0.04	0.09	1.61	132
	16-18	1.14	2.23	0.03	2.71	5.30	0.07	0.35	0.20	0.04	0.1	1.51	128
	18-20	1.77	3.44	0.05	3.47	6.72	0.07	0.30	0.19	0.04	0.08	1.59	127
	20-22	1.59	3.24	0.05	4.35	8.88	0.07	0.30	0.24	0.04	0.06	1.33	88.7
	22-24	1.51	3.09	0.05	4.90	10.0	0.07	0.28	0.23	0.04	0.06	1.32	87.7

APPENDIX L

Formyl- and carboxy- lignin-phenol proxies and yields normalized to g dry sediment (Σ) and 100 mg OC (Λ) of Fiordland, NZ vegetation and soils.

Sample	Σ5f	Σ5c	Σ6c	Σ2c	ΣcV	Λ5f	Λ5c	Λ6c	Λ2c	ΛcV	cV/V
SUW-1	0.56	1.78	0.04	0.55	2.93	0.14	0.43	0.01	0.14	0.72	0.08
SUW-2	0.72	2.50	0.06	0.72	3.99	0.17	0.59	0.01	0.17	0.95	0.11
SUW-3	0.66	4.25	0.07	1.02	5.99	0.21	1.38	0.02	0.33	1.94	0.09
AW-MH	0.19	0.33	0.01	0.07	0.61	0.04	0.07	0.00	0.01	0.13	0.04
AW-SB	0.62	0.54	0.00	0.21	1.37	0.14	0.12	0.00	0.05	0.30	0.08
GW-T	0.39	2.43	0.07	0.90	3.80	0.08	0.49	0.01	0.18	0.77	0.06
AB-SB	0.00	0.34	0.00	0.00	0.34	0.00	0.06	0.00	0.00	0.06	0.04
GB-T	0.23	1.69	0.02	0.33	2.26	0.04	0.33	0.00	0.06	0.44	0.06
AL-MH	0.02	0.09	0.00	0.00	0.11	0.00	0.02	0.00	0.00	0.02	0.04
$AL\text{-}SB_G$	0.22	0.59	0.00	0.18	0.99	0.04	0.12	0.00	0.03	0.19	0.05
$AL\text{-}SB_B$	0.24	0.93	0.00	0.22	1.39	0.05	0.18	0.00	0.04	0.27	0.08
$AL\text{-}FF_{AG}$	0.01	0.21	0.00	0.00	0.22	0.00	0.05	0.00	0.00	0.05	0.05
$AL\text{-}FF_{FY}$	0.07	0.38	0.00	0.06	0.51	0.02	0.09	0.00	0.01	0.12	0.06
$AL\text{-}FF_{FB}$	0.06	0.24	0.03	0.00	0.33	0.01	0.05	0.01	0.00	0.07	0.05
GN-T	0.12	0.55	0.02	0.03	0.72	0.02	0.11	0.00	0.01	0.14	0.05
LL	0.27	1.41	0.02	0.28	1.98	0.06	0.32	0.00	0.06	0.45	0.09
F-NW	0.05	0.73	0.01	0.13	0.91	0.01	0.15	0.00	0.03	0.19	0.07
F-W	0.27	1.52	0.00	0.40	2.19	0.06	0.33	0.00	0.09	0.47	0.05
M	0.01	0.18	0.00	0.03	0.22	0.00	0.06	0.00	0.01	0.07	0.09
G	0.04	0.12	0.00	0.02	0.19	0.01	0.03	0.00	0.01	0.04	0.04
E-1	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.04
E-2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.03
S-GA1	0.01	0.10	0.00	0.01	0.12	0.03	0.31	0.01	0.05	0.40	0.27
S-GA2	0.00	0.06	0.00	0.01	0.07	0.02	0.27	0.01	0.03	0.33	0.32
S-DC1	0.01	0.07	0.00	0.01	0.09	0.02	0.16	0.00	0.03	0.21	0.23
S-DC2	0.08	0.72	0.01	0.12	0.93	0.06	0.50	0.01	0.08	0.64	0.15
S-DC3	0.00	0.01	0.00	0.00	0.02	0.02	0.18	0.01	0.02	0.23	0.12
S-DS	0.13	1.21	0.01	0.18	1.52	0.03	0.29	0.00	0.04	0.36	0.18
S-PI1	0.21	1.54	0.03	0.25	2.02	0.04	0.30	0.01	0.05	0.39	0.13
S-PI2	0.26	1.80	0.05	0.34	2.44	0.07	0.51	0.01	0.09	0.69	0.12

APPENDIX M

Formyl- and carboxy- lignin-phenol proxies and yields normalized to g dry sediment (Σ) and 100 mg OC (Λ) of Fiordland, NZ sediments.

Core	Depth (cm)	Σ5f	Σ5c	Σ6c	Σ2c	ΣcV	Λ5f	Λ5c	Λ6c	Λ2c	ΛcV	cV/V
MR2	0-2	0.01	0.18	0.00	0.03	0.23	0.03	0.44	0.01	0.08	0.56	0.10
	2-4	0.01	0.10	0.00	0.03	0.15	0.03	0.25	0.01	0.09	0.37	0.19
	4-6	0.02	0.15	0.01	0.05	0.23	0.05	0.39	0.02	0.13	0.58	0.17
	8-10	0.01	0.08	0.00	0.03	0.12	0.02	0.22	0.01	0.07	0.33	0.18
	10-12	0.01	0.08	0.00	0.03	0.12	0.03	0.21	0.01	0.07	0.32	0.18
	12-14	0.01	0.11	0.00	0.02	0.14	0.02	0.30	0.00	0.07	0.39	0.11
	14-16	0.01	0.06	0.00	0.02	0.10	0.03	0.18	0.01	0.06	0.28	0.17
	16-18	0.00	0.05	0.00	0.02	0.07	0.01	0.14	0.01	0.06	0.21	0.15
	18-20	0.01	0.11	0.01	0.04	0.16	0.04	0.30	0.02	0.10	0.46	0.19
	20-22	0.01	0.09	0.00	0.02	0.11	0.03	0.24	0.00	0.04	0.32	0.14
CA4	2-4	0.03	0.25	0.00	0.04	0.32	0.04	0.32	0.00	0.04	0.41	0.11
	4-6	0.03	0.30	0.01	0.06	0.40	0.03	0.28	0.01	0.05	0.37	0.09
	6-8	0.02	0.33	0.00	0.06	0.41	0.02	0.33	0.00	0.06	0.41	0.09
	8-10	0.01	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.01	0.00
	22-24	0.02	0.15	0.00	0.03	0.20	0.05	0.34	0.00	0.06	0.45	0.11
	24-26	0.02	0.12	0.00	0.02	0.17	0.05	0.28	0.00	0.06	0.38	0.12
	26-28	0.03	0.20	0.00	0.03	0.26	0.06	0.43	0.00	0.07	0.56	0.15
	30-32	0.02	0.13	0.00	0.02	0.18	0.07	0.51	0.01	0.09	0.68	0.12
	34-36	0.07	0.38	0.01	0.07	0.53	0.08	0.44	0.01	0.08	0.61	0.12
	36-38	0.05	0.30	0.00	0.06	0.41	0.06	0.35	0.00	0.07	0.48	0.12
DC1	0-2	0.00	0.03	0.00	0.00	0.03	0.00	0.03	0.00	0.00	0.03	0.01
	2-4	0.04	0.28	0.00	0.06	0.38	0.04	0.32	0.00	0.07	0.44	0.11
	4-6	0.03	0.24	0.01	0.06	0.33	0.05	0.39	0.01	0.10	0.54	0.17
	6-8	0.02	0.34	0.01	0.06	0.43	0.04	0.48	0.01	0.09	0.61	0.08
	8-10	0.04	0.23	0.01	0.09	0.38	0.05	0.29	0.02	0.11	0.46	0.13
	10-12	0.03	0.23	0.00	0.06	0.32	0.04	0.31	0.00	0.08	0.43	0.08
	12-14	0.02	0.24	0.00	0.05	0.31	0.02	0.24	0.00	0.05	0.31	0.10
	14-16	0.04	0.31	0.02	0.09	0.46	0.03	0.28	0.01	0.08	0.40	0.17
	16-18	0.02	0.10	0.01	0.01	0.14	0.02	0.10	0.00	0.01	0.13	0.05
	18-20	0.02	0.06	0.00	0.00	0.08	0.01	0.05	0.00	0.00	0.07	0.03
	20-22	0.05	0.29	0.02	0.11	0.47	0.06	0.35	0.03	0.13	0.57	0.14
	22-24	0.02	0.16	0.00	0.03	0.21	0.02	0.21	0.00	0.04	0.27	0.11
	24-26	0.01	0.13	0.00	0.00	0.15	0.02	0.16	0.00	0.00	0.18	0.07
	26-28	0.02	0.19	0.00	0.01	0.23	0.03	0.23	0.00	0.01	0.27	0.11
	28-30	0.05	0.29	0.00	0.05	0.38	0.05	0.29	0.00	0.05	0.39	0.12
	30-32	0.01	0.08	0.00	0.00	0.09	0.02	0.08	0.00	0.00	0.10	0.05
	32-34	0.05	0.30	0.00	0.05	0.40	0.05	0.31	0.00	0.05	0.42	0.12
	34-36	0.05	0.29	0.00	0.05	0.39	0.05	0.31	0.00	0.05	0.42	0.12
	36-38	0.04	0.27	0.00	0.04	0.35	0.04	0.29	0.00	0.05	0.38	0.13
	40-42	0.04	0.29	0.00	0.05	0.39	0.05	0.35	0.00	0.06	0.46	0.14
	42-44	0.03	0.20	0.00	0.03	0.26	0.04	0.28	0.00	0.04	0.37	0.14
BA1	0-2	0.03	0.23	0.00	0.05	0.31	0.04	0.38	0.00	0.08	0.51	0.11
	2-4	0.02	0.08	0.00	0.02	0.12	0.05	0.18	0.00	0.04	0.27	0.09
	4-6	0.02	0.13	0.01	0.00	0.16	0.04	0.29	0.02	0.00	0.34	0.13
	6-8	0.02	0.17	0.00	0.03	0.22	0.03	0.32	0.01	0.06	0.42	0.09
	8-10	0.02	0.19	0.01	0.02	0.25	0.04	0.34	0.01	0.03	0.44	0.12
	10-12	0.03	0.22	0.00	0.03	0.29	0.05	0.36	0.00	0.05	0.46	0.12
	12-14	0.03	0.25	0.00	0.03	0.32	0.05	0.44	0.00	0.05	0.55	0.13
	14-16	0.04	0.26	0.00	0.05	0.34	0.06	0.43	0.00	0.07	0.57	0.15
	16-18	0.03	0.25	0.00	0.04	0.33	0.05	0.41	0.00	0.07	0.54	0.15
	18-20	0.02	0.18	0.00	0.03	0.23	0.04	0.32	0.00	0.05	0.42	0.13
SC2	0-2	0.01	0.09	0.00	0.00	0.11	0.03	0.27	0.01	0.01	0.32	0.13
	2-4	0.01	0.05	0.00	0.01	0.07	0.05	0.27	0.02	0.04	0.38	0.17
	4-6	0.02	0.18	0.02	0.06	0.27	0.04	0.28	0.03	0.09	0.43	0.18
	6-8	0.03	0.27	0.03	0.09	0.42	0.05	0.43	0.04	0.14	0.66	0.18
LS1	0-2	0.00	0.06	0.00	0.02	0.09	0.01	0.13	0.00	0.05	0.19	0.16
	2-4	0.01	0.10	0.01	0.04	0.15	0.02	0.21	0.01	0.08	0.32	0.20
	4-6	0.01	0.08	0.00	0.03	0.13	0.03	0.20	0.01	0.07	0.31	0.18
	6-8	0.01	0.07	0.01	0.03	0.12	0.03	0.21	0.02	0.08	0.34	0.19
	8-10	0.01	0.07	0.00	0.01	0.09	0.02	0.20	0.00	0.03	0.26	0.12
	10-12	0.01	0.06	0.00	0.02	0.09	0.01	0.14	0.01	0.05	0.21	0.16
	12-14	0.01	0.08	0.00	0.03	0.12	0.02	0.21	0.01	0.07	0.32	0.20
	14-16	0.01	0.07	0.00	0.03	0.11	0.02	0.20	0.01	0.07	0.31	0.19
	16-18	0.00	0.06	0.00	0.02	0.09	0.01	0.14	0.01	0.06	0.22	0.16
	18-20	0.02	0.11	0.01	0.04	0.17	0.03	0.21	0.01	0.08	0.33	0.19
	20-22	0.00	0.05	0.00	0.01	0.06	0.01	0.12	0.00	0.01	0.14	0.11
	22-24	0.01	0.08	0.00	0.01	0.10	0.04	0.25	0.00	0.05	0.34	0.14

APPENDIX N

Lignin-Dimer proxies and yields normalized to g dry sediment (Σ) and 100 mg OC (Λ) of Fiordland, NZ vegetation and soils.

Sample	ΣD	Σ5,5'	Σβ,1	Σα,1	Σα,5	Σ4-O-5'	ΛD	Λ5,5'	Λβ,1	Λα,1	Λα,5	Λ4-O-5'	SR/RR	(β1+α1)/(α2+α5)	D/M
SUW-1	10.0	4.15	2.94	0.75	0.40	1.75	2.44	1.01	0.72	0.18	0.10	0.43	1.41	1.72	0.22
SUW-2	15.0	7.56	2.20	2.01	0.59	2.61	3.55	1.79	0.52	0.48	0.14	0.62	0.98	1.31	0.13
SUW-3	21.9	13.0	4.04	0.66	1.19	3.00	7.10	4.21	1.31	0.21	0.39	0.97	0.68	1.12	0.16
AW-MH	6.92	5.62	0.55	0.27	0.11	0.38	1.43	1.16	0.11	0.06	0.02	0.08	0.23	1.71	0.12
AW-SB	5.23	0.71	2.22	0.96	0.08	1.26	1.15	0.16	0.49	0.21	0.02	0.28	6.45	2.36	0.05
GW-T	22.0	15.3	4.47	0.26	1.35	0.58	4.45	3.10	0.90	0.05	0.27	0.12	0.43	2.43	0.32
AB-SB	16.3	15.1	0.61	0.17	0.16	0.26	2.71	2.51	0.10	0.03	0.03	0.04	0.08	1.87	1.00
GB-T	10.3	7.80	1.21	0.33	0.55	0.39	1.99	1.51	0.23	0.06	0.11	0.08	0.32	1.65	0.24
AL-MH	0.82	0.59	0.11	0.05	0.02	0.06	0.16	0.12	0.02	0.01	0.00	0.01	0.39	2.05	0.12
AL-SB_G	4.44	2.87	0.72	0.12	0.21	0.52	0.87	0.56	0.14	0.02	0.04	0.10	0.55	1.16	0.08
AL-SB_B	4.54	2.93	0.66	0.10	0.30	0.55	0.87	0.56	0.13	0.02	0.06	0.11	0.55	0.89	0.10
AL-FF_{AG}	0.73	0.62	0.11	0.00	0.00	0.00	0.16	0.14	0.03	0.00	0.00	0.00	0.18	N/A	0.10
AL-FF_{FY}	1.27	0.91	0.25	0.00	0.00	0.10	0.30	0.22	0.06	0.00	0.00	0.03	0.40	2.43	0.07
AL-FF_{FB}	3.63	3.32	0.14	0.05	0.00	0.12	0.74	0.67	0.03	0.01	0.00	0.02	0.09	1.58	0.22
GN-T	4.21	3.12	0.70	0.22	0.13	0.04	0.84	0.62	0.14	0.04	0.03	0.01	0.35	7.37	0.20
LL	6.65	4.65	0.86	0.21	0.34	0.60	1.51	1.05	0.20	0.05	0.08	0.14	0.43	1.15	0.14
F-NW	3.35	2.75	0.33	0.07	0.16	0.05	0.70	0.57	0.07	0.01	0.03	0.01	0.22	1.91	0.23
F-W	9.73	7.24	1.60	0.24	0.46	0.18	2.08	1.55	0.34	0.05	0.10	0.04	0.34	2.89	0.20
M	0.35	0.35	0.00	0.00	0.00	0.00	0.11	0.11	0.00	0.00	0.00	0.00	0.00	N/A	0.07
G	0.76	0.24	0.18	0.12	0.02	0.20	0.17	0.05	0.04	0.03	0.01	0.05	2.17	1.27	0.05
E-1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	N/A	N/A	0.00
E-2	0.03	0.03	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	N/A	0.21
S-GA1	0.13	0.13	0.00	0.00	0.00	0.00	0.43	0.43	0.00	0.00	0.00	0.00	0.00	N/A	0.16
S-GA2	0.13	0.06	0.01	0.05	0.00	0.00	0.63	0.30	0.04	0.26	0.01	0.02	1.10	10.4	0.25
S-DC1	0.10	0.09	0.01	0.00	0.00	0.00	0.23	0.21	0.01	0.00	0.00	0.00	0.06	N/A	0.14
S-DC2	1.73	1.10	0.12	0.32	0.10	0.10	1.20	0.76	0.08	0.22	0.07	0.07	0.57	2.27	0.17
S-DC3	0.03	0.02	0.00	0.00	0.00	0.00	0.33	0.28	0.03	0.00	0.01	0.00	0.17	2.43	0.09
S-DS	4.50	3.42	0.18	0.63	0.12	0.15	1.07	0.81	0.04	0.15	0.03	0.04	0.34	4.81	0.31
S-PI1	6.34	4.15	0.33	1.38	0.12	0.35	1.23	0.81	0.06	0.27	0.02	0.07	0.53	3.60	0.22
S-PI2	5.68	4.63	0.32	0.11	0.26	0.37	1.60	1.30	0.09	0.03	0.07	0.10	0.23	0.69	0.16

APPENDIX O

Lignin-Dimer proxies and yields normalized to g dry sediment (Σ) and 100 mg OC (Λ) of Fiordland, NZ sediments.

Core	Depth (cm)	ΣD	Σ5,5'	Σβ,1	Σα,1	Σα,5	Σ4-O-5'	ΛD	Λ5,5'	Λβ,1	Λα,1	Λα,5	Λ4-O-5'	SR/RR	(β1+α1)/(α2+α5)	D/M
MR2	0-2	0.31	0.24	0.03	0.00	0.02	0.03	0.76	0.58	0.07	0.00	0.04	0.08	0.32	0.62	0.06
	2-4	0.26	0.17	0.04	0.01	0.02	0.03	0.65	0.42	0.11	0.02	0.04	0.07	0.56	1.09	0.13
	4-6	0.40	0.28	0.04	0.01	0.02	0.04	1.02	0.73	0.11	0.02	0.05	0.11	0.40	0.85	0.13
	8-10	0.20	0.13	0.02	0.01	0.01	0.03	0.53	0.37	0.07	0.01	0.02	0.07	0.46	0.95	0.12
	10-12	0.19	0.13	0.02	0.01	0.01	0.02	0.50	0.35	0.05	0.01	0.03	0.06	0.45	0.76	0.11
	12-14	0.23	0.16	0.02	0.00	0.02	0.04	0.64	0.44	0.05	0.00	0.05	0.10	0.45	0.29	0.07
	14-16	0.18	0.15	0.01	0.00	0.00	0.01	0.50	0.41	0.03	0.01	0.01	0.03	0.21	0.96	0.11
	16-18	0.11	0.08	0.01	0.00	0.00	0.01	0.31	0.22	0.04	0.00	0.01	0.03	0.38	1.00	0.08
	18-20	0.31	0.19	0.03	0.01	0.03	0.05	0.86	0.54	0.08	0.04	0.07	0.14	0.61	0.55	0.14
	20-22	0.21	0.14	0.01	0.03	0.01	0.02	0.60	0.40	0.02	0.09	0.03	0.07	0.51	1.15	0.11
CA4	2-4	0.79	0.48	0.04	0.17	0.03	0.08	1.00	0.61	0.05	0.21	0.04	0.10	0.55	1.36	0.11
	4-6	0.92	0.61	0.08	0.05	0.07	0.11	0.85	0.57	0.08	0.04	0.06	0.10	0.51	0.75	0.09
	6-8	0.64	0.50	0.04	0.02	0.01	0.07	0.65	0.50	0.04	0.02	0.01	0.07	0.30	0.67	0.06
	8-10	0.03	0.03	0.00	0.00	0.00	0.00	0.05	0.05	0.00	0.00	0.00	0.00	0.00	N/A	0.01
	22-24	0.57	0.33	0.05	0.06	0.08	0.05	1.26	0.73	0.11	0.13	0.17	0.12	0.75	0.83	0.12
	24-26	0.44	0.32	0.03	0.01	0.02	0.06	1.02	0.75	0.07	0.03	0.05	0.13	0.37	0.53	0.12
	26-28	0.63	0.40	0.04	0.09	0.04	0.06	1.39	0.89	0.09	0.19	0.09	0.14	0.57	1.24	0.16
	30-32	0.51	0.33	0.05	0.05	0.04	0.05	1.96	1.25	0.18	0.18	0.14	0.21	0.57	1.06	0.15
	34-36	1.75	0.98	0.21	0.23	0.08	0.25	2.03	1.14	0.25	0.27	0.09	0.29	0.79	1.35	0.13
	36-38	1.26	0.70	0.13	0.19	0.06	0.18	1.48	0.83	0.16	0.22	0.07	0.21	0.80	1.35	0.14
DC1	0-2	0.49	0.44	0.04	0.00	0.00	0.00	0.56	0.51	0.05	0.00	0.00	0.00	0.10	N/A	0.07
	2-4	0.35	0.31	0.02	0.00	0.00	0.03	0.41	0.35	0.02	0.00	0.00	0.03	0.15	0.53	0.04
	4-6	0.82	0.52	0.10	0.04	0.06	0.10	1.34	0.85	0.17	0.06	0.09	0.17	0.59	0.89	0.17
	6-8	1.14	0.82	0.12	0.02	0.09	0.09	1.62	1.17	0.17	0.03	0.13	0.13	0.39	0.74	0.09
	8-10	1.07	0.72	0.13	0.05	0.06	0.11	1.32	0.88	0.16	0.06	0.08	0.14	0.50	1.01	0.16
	10-12	0.76	0.57	0.06	0.03	0.04	0.07	1.03	0.77	0.08	0.04	0.05	0.09	0.34	0.78	0.09
	12-14	0.87	0.65	0.07	0.03	0.05	0.08	0.87	0.65	0.07	0.03	0.05	0.08	0.34	0.81	0.12
	14-16	1.35	1.02	0.11	0.05	0.06	0.10	1.19	0.90	0.10	0.05	0.06	0.09	0.32	1.01	0.19
	16-18	0.41	0.38	0.02	0.01	0.00	0.01	0.39	0.36	0.02	0.01	0.00	0.01	0.08	2.52	0.06
	18-20	1.87	1.78	0.01	0.05	0.03	0.00	1.65	1.56	0.01	0.05	0.02	0.00	0.05	2.48	0.31
	20-22	1.15	0.72	0.16	0.06	0.07	0.13	1.37	0.87	0.19	0.07	0.08	0.16	0.58	1.07	0.15
	22-24	0.37	0.28	0.02	0.00	0.02	0.05	0.49	0.37	0.03	0.00	0.02	0.07	0.32	0.31	0.08
	24-26	0.48	0.31	0.03	0.10	0.01	0.03	0.57	0.37	0.03	0.12	0.01	0.03	0.53	3.39	0.10
	26-28	0.55	0.38	0.07	0.01	0.02	0.07	0.65	0.44	0.08	0.01	0.03	0.08	0.46	0.90	0.10
	28-30	0.78	0.54	0.06	0.02	0.05	0.11	0.79	0.55	0.06	0.02	0.05	0.11	0.44	0.48	0.10
	30-32	0.56	0.40	0.07	0.01	0.03	0.06	0.60	0.43	0.08	0.01	0.03	0.06	0.42	0.95	0.12
	32-34	0.85	0.59	0.07	0.03	0.06	0.11	0.90	0.62	0.07	0.03	0.06	0.11	0.44	0.58	0.11
	34-36	0.82	0.57	0.09	0.01	0.05	0.10	0.87	0.61	0.10	0.01	0.05	0.10	0.43	0.70	0.11
	36-38	0.70	0.48	0.07	0.02	0.04	0.09	0.77	0.52	0.08	0.02	0.04	0.10	0.47	0.73	0.11
	40-42	0.80	0.54	0.07	0.02	0.06	0.11	0.96	0.65	0.09	0.03	0.07	0.13	0.48	0.59	0.12
	42-44	0.52	0.38	0.04	0.01	0.04	0.06	0.74	0.53	0.05	0.01	0.05	0.09	0.38	0.50	0.12
BA1	0-2	0.39	0.31	0.02	0.00	0.01	0.04	0.64	0.51	0.04	0.00	0.02	0.07	0.24	0.39	0.06
	2-4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	N/A	N/A	0.00
	4-6	0.37	0.24	0.05	0.01	0.02	0.06	0.81	0.53	0.10	0.01	0.04	0.13	0.53	0.73	0.12
	6-8	0.55	0.37	0.05	0.01	0.06	0.06	1.06	0.71	0.10	0.03	0.11	0.11	0.49	0.56	0.09
	8-10	0.53	0.33	0.06	0.02	0.03	0.08	0.96	0.59	0.12	0.03	0.06	0.15	0.62	0.68	0.11
	10-12	0.64	0.40	0.06	0.01	0.09	0.08	1.04	0.64	0.09	0.02	0.15	0.13	0.57	0.45	0.12
	12-14	0.62	0.40	0.05	0.03	0.04	0.10	1.07	0.69	0.08	0.05	0.07	0.18	0.54	0.49	0.11
	14-16	0.80	0.44	0.07	0.13	0.06	0.10	1.31	0.73	0.12	0.21	0.09	0.17	0.81	1.25	0.15
	16-18	0.76	0.42	0.07	0.12	0.05	0.11	1.25	0.69	0.11	0.20	0.08	0.17	0.82	1.25	0.15
	18-20	0.51	0.33	0.03	0.04	0.03	0.08	0.92	0.59	0.05	0.08	0.06	0.14	0.56	0.63	0.12
SC2	0-2	0.07	0.07	0.00	0.00	0.00	0.00	0.21	0.20	0.01	0.00	0.00	0.01	0.04	N/A	0.03
	2-4	0.17	0.13	0.02	0.00	0.01	0.02	0.88	0.65	0.10	0.00	0.03	0.11	0.37	0.70	0.16
	4-6	0.58	0.37	0.08	0.02	0.04	0.06	0.92	0.59	0.12	0.04	0.07	0.10	0.57	0.94	0.15
	6-8	0.86	0.52	0.12	0.04	0.07	0.11	1.35	0.82	0.19	0.06	0.11	0.17	0.64	0.90	0.14
LS1	0-2	0.15	0.11	0.02	0.00	0.01	0.01	0.31	0.24	0.03	0.00	0.02	0.02	0.29	0.97	0.10
	2-4	0.25	0.17	0.04	0.01	0.01	0.03	0.54	0.37	0.08	0.02	0.01	0.07	0.46	1.22	0.13
	4-6	0.23	0.15	0.04	0.01	0.01	0.03	0.57	0.37	0.09	0.02	0.02	0.07	0.52	1.14	0.13
	6-8	0.23	0.15	0.04	0.01	0.01	0.03	0.68	0.44	0.11	0.02	0.04	0.08	0.57	1.19	0.14
	8-10	0.18	0.11	0.01	0.02	0.01	0.02	0.49	0.32	0.03	0.07	0.03	0.05	0.47	0.93	0.09
	10-12	0.15	0.10	0.02	0.00	0.00	0.01	0.36	0.26	0.06	0.01	0.01	0.02	0.42	2.08	0.10
	12-14	0.21	0.14	0.03	0.01	0.01	0.03	0.56	0.37	0.08	0.01	0.03	0.07	0.52	0.96	0.13
	14-16	0.19	0.12	0.03	0.00	0.01	0.02	0.52	0.34	0.08	0.01	0.03	0.06	0.55	1.02	0.12
	16-18	0.17	0.12	0.03	0.00	0.00	0.02	0.40	0.28	0.07	0.00	0.01	0.04	0.43	1.66	0.11
	18-20	0.29	0.19	0.04	0.01	0.01	0.04	0.57	0.37	0.09	0.02	0.02	0.08	0.54	1.04	0.12
	20-22	0.08	0.07	0.00	0.00	0.01	0.01	0.22	0.17	0.01	0.00	0.02	0.02	0.24	0.18	0.08
	22-24	0.18	0.13	0.01	0.00	0.01	0.03	0.58	0.43	0.03	0.00	0.04	0.09	0.36	0.21	0.10

APPENDIX P

Cutin hydroxy acid proxies and yields normalized to g dry sediment (Σ) and 100 mg OC (Λ) of Fiordland, NZ vegetation and soils.

Sample	ΣC_A	ΣC_{16}	ΣC_{18}	ΛC_A	ΛC_{16}	ΛC_{18}	ω-$C_{16}/\Sigma C_A$	x,ω-C16/ΣC_A	9,10,ω-$C_{18}/\Sigma C_A$	8-OH	9-OH
SUW-1	0.05	0.05	0.00	0.01	0.01	0.00	0.00	1.00	0.00	0.00	0.00
SUW-2	0.04	0.04	0.00	0.01	0.01	0.00	0.00	1.00	0.00	0.00	0.00
SUW-3	0.04	0.03	0.01	0.01	0.01	0.00	0.00	0.77	0.23	0.00	0.00
AW-MH	20.5	17.5	3.05	4.22	3.59	0.63	0.08	0.69	0.01	0.03	0.04
AW-SB	0.19	0.19	0.00	0.04	0.04	0.00	0.00	1.00	0.00	0.00	0.00
GW-T	0.19	0.19	0.00	0.04	0.04	0.00	0.00	0.00	0.00	0.00	0.00
AB-SB	20.7	16.5	4.17	3.45	2.75	0.70	0.10	0.27	0.00	0.48	0.28
GB-T	6.54	5.84	0.71	1.27	1.13	0.14	0.10	0.55	0.02	0.03	0.11
AL-MH	1.75	1.69	0.06	0.35	0.34	0.01	0.14	0.14	0.02	0.00	0.00
AL-SB_G	47.4	47.3	0.08	9.26	9.24	0.01	0.01	0.92	0.00	0.05	0.03
AL-SB_B	62.3	62.3	0.00	11.9	11.9	0.00	0.01	0.93	0.00	0.04	0.04
AL-FF_{AG}	13.7	5.24	8.49	3.07	1.17	1.90	0.01	0.33	0.60	0.45	0.36
AL-FF_{FY}	13.6	8.6	4.95	3.25	2.07	1.19	0.01	0.46	0.36	0.05	0.92
AL-FF_{FB}	59.2	58.9	0.21	12.00	11.96	0.04	0.04	0.84	0.00	0.05	0.35
GN-T	19.4	19.3	0.08	3.88	3.86	0.02	0.00	1.06	0.00	0.03	0.07
LL	14.1	10.6	3.49	3.19	2.40	0.79	0.04	0.61	0.20	0.07	0.05
F-NW	1.51	1.51	0.00	0.32	0.32	0.00	0.90	0.96	0.00	0.00	0.00
F-W	0.41	0.41	0.00	0.09	0.09	0.00	0.72	1.00	0.00	0.00	0.00
M	0.37	0.32	0.05	0.12	0.10	0.02	0.38	0.87	0.13	0.00	0.24
G	1.29	0.29	1.00	0.28	0.06	0.22	0.04	0.21	0.60	0.19	0.71
E-1	2.15	2.15	0.00	0.56	0.56	0.00	0.00	1.00	0.00	0.04	0.03
E-2	0.03	0.03	0.00	0.01	0.01	0.00	0.74	1.00	0.00	0.00	0.00
S-GA1	0.49	0.39	0.11	1.60	1.25	0.34	0.05	0.58	0.21	0.06	0.15
S-GA2	0.38	0.25	0.12	1.82	1.22	0.60	0.05	0.51	0.33	0.07	0.12
S-DC1	0.33	0.20	0.13	0.79	0.49	0.31	0.08	0.50	0.39	0.10	0.25
S-DC2	1.20	1.07	0.13	0.79	0.71	0.09	0.10	0.73	0.09	0.08	0.21
S-DC3	0.08	0.07	0.01	1.01	0.92	0.10	0.06	0.80	0.09	0.06	0.22
S-DS	72.5	67.5	5.03	17.8	16.4	1.40	0.02	0.26	0.17	0.17	0.14
S-PI1	19.2	18.0	1.21	3.73	3.49	0.23	0.05	0.78	0.05	0.05	0.24
S-PI2	11.4	10.7	0.73	3.20	2.99	0.20	0.06	0.78	0.05	0.05	0.25

APPENDIX Q

Cutin hydroxy acid proxies and yields normalized to g dry sediment (Σ) and 100 mg OC (Λ) of Fiordland, NZ sediments.

Core	Depth (cm)	ΣC_A	ΣC_{16}	ΣC_{18}	ΛC_A	ΛC_{16}	ΛC_{18}	ω-C_{16}/ΣC_{16}	ω-C16/Σ(ω,ω-C_{18}/Σ	8-OH	9-OH
MR2	0-2	0.18	0.15	0.03	0.43	0.36	0.07	0.08	0.55	0.16	0.08	0.10
	2-4	0.49	0.40	0.09	1.22	1.00	0.21	0.04	0.68	0.18	0.06	0.13
	4-6	0.74	0.55	0.19	1.91	1.42	0.49	0.04	0.61	0.25	0.06	0.14
	8-10	0.35	0.29	0.06	0.95	0.79	0.16	0.04	0.67	0.17	0.07	0.14
	10-12	0.39	0.33	0.06	1.05	0.88	0.17	0.05	0.69	0.16	0.06	0.14
	12-14	0.15	0.12	0.03	0.42	0.34	0.08	0.03	0.63	0.19	0.07	0.16
	14-16	0.37	0.31	0.07	1.05	0.86	0.19	0.12	0.70	0.18	0.06	0.13
	16-18	0.32	0.27	0.05	0.92	0.77	0.15	0.05	0.69	0.17	0.07	0.13
	18-20	0.27	0.22	0.05	0.76	0.62	0.14	0.03	0.54	0.18	0.06	0.13
	20-22	0.40	0.31	0.09	1.12	0.87	0.25	0.04	0.64	0.22	0.07	0.12
CA4	2-4	1.72	1.23	0.49	2.19	1.57	0.63	0.05	0.59	0.26	0.08	0.10
	4-6	1.05	0.73	0.33	0.98	0.67	0.31	0.04	0.46	0.31	0.08	0.12
	6-8	0.52	0.45	0.07	0.53	0.45	0.07	0.06	0.55	0.14	0.08	0.12
	8-10	0.32	0.32	0.00	0.47	0.47	0.00	0.11	0.84	0.00	0.07	0.09
	22-24	1.28	0.88	0.41	2.85	1.95	0.90	0.04	0.55	0.31	0.07	0.08
	24-26	1.70	1.09	0.61	3.94	2.53	1.41	0.04	0.53	0.35	0.10	0.10
	26-28	1.87	1.18	0.69	4.13	2.61	1.52	0.04	0.51	0.36	0.06	0.07
	30-32	1.35	0.86	0.49	5.14	3.28	1.87	0.04	0.52	0.35	0.07	0.09
	34-36	1.77	0.93	0.85	2.06	1.08	0.98	0.06	0.40	0.44	0.08	0.08
	36-38	1.82	0.72	1.10	2.14	0.85	1.29	0.04	0.32	0.56	0.08	0.13
DC1	0-2	2.49	1.99	0.50	2.86	2.28	0.58	0.04	0.65	0.20	0.08	0.11
	2-4	0.42	0.39	0.03	0.49	0.45	0.04	0.12	0.58	0.06	0.02	0.14
	4-6	1.01	0.78	0.23	1.65	1.28	0.37	0.06	0.47	0.21	0.07	0.12
	6-8	0.87	0.59	0.28	1.24	0.84	0.40	0.04	0.47	0.31	0.09	0.11
	8-10	3.80	2.76	1.04	4.69	3.40	1.28	0.03	0.59	0.26	0.06	0.09
	10-12	1.43	1.19	0.24	1.94	1.62	0.32	0.05	0.65	0.15	0.06	0.09
	12-14	2.45	1.74	0.71	2.44	1.73	0.71	0.04	0.51	0.28	0.06	0.08
	14-16	2.79	1.73	1.06	2.47	1.53	0.93	0.11	0.41	0.37	0.06	0.09
	16-18	2.36	2.20	0.16	2.21	2.06	0.15	0.06	0.72	0.05	0.07	0.10
	18-20	2.48	2.35	0.13	2.18	2.07	0.11	0.07	0.76	0.03	0.07	0.11
	20-22	1.69	1.08	0.62	2.02	1.29	0.74	0.03	0.45	0.36	0.07	0.10
	22-24	1.34	1.00	0.34	1.76	1.32	0.45	0.05	0.65	0.25	0.07	0.10
	24-26	2.29	1.69	0.60	2.72	2.00	0.71	0.04	0.63	0.26	0.07	0.11
	26-28	2.26	1.69	0.57	2.67	1.99	0.68	0.04	0.63	0.25	0.07	0.10
	28-30	1.90	1.45	0.45	1.93	1.47	0.46	0.04	0.64	0.23	0.07	0.11
	30-32	3.52	2.40	1.11	3.78	2.58	1.20	0.03	0.57	0.31	0.08	0.10
	32-34	2.94	2.31	0.62	3.10	2.44	0.66	0.03	0.66	0.21	0.07	0.10
	34-36	3.97	2.72	1.26	4.22	2.89	1.34	0.03	0.57	0.31	0.08	0.11
	36-38	2.57	1.79	0.77	2.83	1.98	0.85	0.03	0.59	0.30	0.08	0.10
	40-42	2.54	1.71	0.84	3.03	2.03	1.00	0.03	0.55	0.32	0.08	0.11
	42-44	4.26	2.72	1.54	6.04	3.85	2.19	0.03	0.51	0.36	0.07	0.10
BA1	0-2	0.22	0.19	0.02	0.36	0.32	0.04	0.06	0.59	0.11	0.00	0.13
	2-4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	4-6	0.43	0.36	0.07	0.94	0.79	0.15	0.04	0.58	0.16	0.06	0.11
	6-8	0.39	0.30	0.09	0.75	0.58	0.17	0.03	0.54	0.23	0.07	0.12
	8-10	0.83	0.65	0.18	1.46	1.14	0.31	0.04	0.60	0.21	0.07	0.11
	10-12	1.22	0.89	0.33	1.97	1.44	0.54	0.04	0.59	0.27	0.06	0.11
	12-14	1.21	0.83	0.38	2.10	1.44	0.66	0.03	0.56	0.31	0.07	0.11
	14-16	1.08	0.75	0.32	1.77	1.24	0.53	0.04	0.56	0.30	0.07	0.11
	16-18	1.13	0.75	0.37	1.85	1.23	0.61	0.04	0.53	0.33	0.06	0.11
	18-20	0.97	0.70	0.27	1.75	1.27	0.48	0.04	0.59	0.28	0.06	0.11
SC2	0-2	0.18	0.18	0.00	0.52	0.51	0.01	0.08	0.68	0.02	0.08	0.09
	2-4	0.40	0.26	0.14	2.06	1.32	0.74	0.04	0.45	0.35	0.07	0.09
	4-6	1.07	0.73	0.34	1.70	1.17	0.54	0.03	0.40	0.31	0.07	0.09
	6-8	1.34	0.92	0.42	2.11	1.45	0.67	0.03	0.40	0.31	0.06	0.10
LS1	0-2	0.69	0.49	0.20	1.46	1.03	0.43	0.04	0.58	0.29	0.06	0.09
	2-4	0.74	0.51	0.23	1.58	1.10	0.49	0.04	0.58	0.30	0.05	0.09
	4-6	0.69	0.46	0.23	1.68	1.12	0.56	0.04	0.55	0.33	0.06	0.09
	6-8	0.56	0.37	0.19	1.64	1.09	0.55	0.04	0.54	0.33	0.06	0.10
	8-10	0.39	0.30	0.10	1.10	0.83	0.27	0.05	0.63	0.24	0.06	0.09
	10-12	0.54	0.38	0.15	1.31	0.94	0.37	0.04	0.58	0.28	0.06	0.09
	12-14	0.65	0.40	0.25	1.73	1.07	0.67	0.03	0.51	0.38	0.06	0.09
	14-16	0.36	0.27	0.09	1.01	0.74	0.26	0.04	0.57	0.26	0.06	0.10
	16-18	0.63	0.44	0.19	1.49	1.05	0.45	0.04	0.58	0.29	0.06	0.09
	18-20	0.80	0.58	0.22	1.57	1.14	0.44	0.03	0.60	0.28	0.06	0.09
	20-22	0.33	0.24	0.09	0.88	0.63	0.25	0.07	0.70	0.20	0.09	0.16
	22-24	0.51	0.37	0.14	1.66	1.19	0.46	0.04	0.58	0.28	0.06	0.09

APPENDIX R

Historical source reconstructions of six sediment cores from Fiordland, NZ.

Core	Depth (cm)	%OMfossil	%OMfossil AVG	%OMterr	%OMmar
MR2	0-2		12.3	42.5	45.2
	2-4		12.3	44.2	43.5
	4-6		12.3	41.8	45.9
	6-8	11	12.3	38.2	49.5
	8-10		12.3	40.6	47.1
	10-12		12.3	41.4	46.3
	12-14		12.3	43.1	44.6
	14-16		12.3	44.3	43.4
	16-18	13.6	12.3	45.4	42.3
	18-20		12.3	45.0	42.7
	20-22		12.3	47.0	40.7
CA4	2-4		8.97	74.1	16.9
	4-6	5.98	8.97	67.3	23.7
	6-8		8.97	68.2	22.8
	8-10		8.97	70.8	20.3
	10-12	15.9	8.97	77.8	13.3
	22-24		8.97	79.9	11.2
	24-26		8.97	80.2	10.8
	26-28		8.97	79.7	11.3
	30-32		8.97	82.0	8.98
	34-36		8.97	85.7	5.30
	36-38		8.97	84.1	6.97
DC1	0-2		4.36	74.5	21.2
	2-4	2.49	4.36	72.5	23.1
	4-6		4.36	74.7	21.0
	6-8		4.36	74.8	20.9
	8-10		4.36	76.3	19.4
	10-12	6.24	4.36	77.9	17.8
	12-14		4.36	75.6	20.1
	14-16		4.36	75.4	20.3
	16-18		4.36	75.6	20.0
	18-20		4.36	76.1	19.5
	20-22		4.36	77.8	17.8
	22-24		4.36	72.4	23.3
	24-26		4.36	71.8	23.8
	26-28		4.36	70.2	25.4
	28-30		4.36	71.6	24.0
	30-32		4.36	70.4	25.3
	32-34		4.36	70.2	25.4
	34-36		4.36	67.0	28.6
	36-38		4.36	67.3	28.4
	40-42		4.36	69.5	26.1
	42-44		4.36	72.9	22.7
BA1	0-2		9.36	61.7	28.9
	2-4	10.8	9.36	63.3	27.3
	4-6	7.94	9.36	61.1	29.5
	6-8		9.36	61.2	29.4
	8-10		9.36	62.7	27.9
	10-12		9.36	62.3	28.4
	12-14		9.36	60.2	30.4
	14-16		9.36	60.8	29.8
	16-18		9.36	58.8	31.8
	18-20		9.36	60.2	30.5
SC2	0-2		10.0	65.6	24.4
	2-4	13.1	10.0	70.3	19.7
	4-6		10.0	70.1	19.9
	6-8	6.94	10.0	68.2	21.8
LS1	0-2		13.8	57.6	28.6
	2-4		13.8	56.3	29.9
	4-6		13.8	56.0	30.2
	6-8	14.5	13.8	57.9	28.3
	8-10		13.8	56.3	29.9
	10-12		13.8	50.2	36.0
	12-14	13.1	13.8	49.4	36.8
	14-16		13.8	54.0	32.2
	16-18		13.8	56.8	29.4
	18-20		13.8	55.1	31.1
	20-22		13.8	57.4	28.8
	22-24		13.8	58.3	27.9

VITA

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